Mechanisms of Deterioration of Nutrients

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ANNUAL REPORT - PHASE V

13 March 1976 - 13 May 1978

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General Introduction

Phase V of this contract was devoted to completion of studies on improved quality freeze-dried foods. In particular studies included the following areas, each of which is covered in a separate section of this Phase V report.

Section 2: Microstructure of Freeze-dried Systems

Previously reported microscopic techniques for study of food microstructure were applied to evaluation of properties of freeze-dried emulsions as a function of emulsion composition.

Section 3: Structural Changes in Freeze-dried Systems

As a result of increases in water content or in temperature, freeze-dried systems may undergo "collapse," a loss of structure resulting in physical changes of importance to quality. Various factors influencing "collapse" were investigated and are reported in this section.

Section 4: Artificial Food Matrices (AFM)

In previous reports we described a process for preparation of fruit-simulating matrices (AFM). Studies on structural properties and organoleptic suitability of these items were continued and are reported in this section.

Section 5: Osmotic Preconcentration to Yield Improved Quality Freeze-dried Products

Studies on osmotic concentration of fruits were expanded to include concentration of vegetable products as a pretreatment

for freeze-drying. Organoleptic evaluations and storage tests were conducted and are reported in this section along with a review of suitability of various osmotic agents as pretreatment before freeze-drying.

2. Microstructure of Freeze-dried Systems

2.1 Introduction

Previously reported microscopic techniques for study of microstructure of freeze-dried multiphase systems were applied to the evaluation of effects of composition on microstructure of freeze-dried emulsions. The results are reported in this section.

2.2 Effect of component composition on microstructure of freeze-dried emulsions

During the course of this study the microstructure of several freeze-dried emulsified model systems was investigated. Results of these investigations were presented at The First International Congress on Engineering and Food in August, 1976. A copy of the manuscript for that paper is presented here. Anticipated publication date of this manuscript in the Proceedings of the First International Congress on Engineering and Food is summer, 1978.[1]

[1] Due to unforseen circumstances, I.C.E.F. was not able to meet its projected plans for publication. This manuscript has now been accepted by the Journal of Food Processing and Preservation and is awaiting publication, some time early Spring, 1979.

Microstructure of Freeze Dried Emulsions: Effect of Emulsion Composition

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ABSTRACT

The physical relationship between lipid and dried solid matrix was studied by microscopic methods. Oil-in-water emulsions were prepared with the lipid concentration and structure-forming solute in the aqueous phase being varied. Methods to quantitatively evaluate the distribution of the lipid phase with respect to the dry matrix material (i.e. encapsulated vs. surface lipid) are presented. The degree of encapsulation of the fat phase in the matrix was shown to depend on morphological characteristics of the solid matrix components and lipid concentration. The microscopic methods reported here also give a picture of the interrelationship of the oil and solid matrix in freeze dried oil-in-water emulsions so that the physical location of fat can be related to product and process parameters. This information will be important for interpreting results of product performance and stability studies, of dried fat-containing food products, and to aid in designing improved dehydrated emulsion-based engineered foods.

INTRODUCTION

The utility of freeze dried multicomponent products, such as emulsified systems, depends on the product being stable during storage and rehydratable to a state which is essentially equal to the original emulsion. The extent to which the quality of the emulsified system is retained in the final product will depend on changes in the interactions between the various components of the multiphase system during the freeze drying process.

Schmidt Walters (1968), Lladser et al (1968) and Lladser and Arancibia (1972) indicate that the physical location of the oil and its interaction with the solid support could be important factors in explaining various properties of freeze dried oil-in-water emulsions. Two extreme cases describing oil locations in a dried emulsion are (1) fully encapsulated as oil globules or (2) thin surface deposits on the solid support (Gejl-Hansen and Flink, 1976; Buma, 1971).

The ratio between free oil and encapsulated oil will determine various physical properties of the dried product such as reconstitutability, stickiness and free flowability of the powdered product, and creaming and foaming behaviour of the rehydrated product. This results since the position of the oil in a given support will determine

the hydrophobic - hydrophilic character of the product and therefore, its wettability and dispersibility (Buma, 1971; Beyerlein, 1972a, 1972b).

To describe the structure of freeze dried oil-in-water emulsions and in particular the location of the oil relative to the support material, it has been necessary to utilize multiple microscopic techniques, as well as to develop some suitable chemical extraction methods (Gejl-Hansen and Flink, 1976). The development of these techniques allows evaluation of the ratio of encapsulated to free fat and the effect that process variables such as oil concentration and solid support material and concentration has on this distribution.

For example, oil concentration relative to solids concentration may influence the ratio between encapsulated fat and free fat. Lladser et al (1968) showed that with higher oil concentration (above 10% oil for 13.3% solids), their emulsion broke during freeze drying. It has been shown that following freeze drying of emulsions containing crystallizing or crystalline solutes, the oil globules are located as a film on the surface of the crystalline solids (Gejl-Hansen and Flink, 1976), whereas it has been shown with lipids (Buma, 1971; Gejl-Hansen and Flink, 1976) and flavor components of low solubility (Flink and Gejl-Hansen, 1972; Flink et al, 1973; Massaldi and King, 1974) that insoluble droplets can be incorporated into an amorphous

matrix during drying processes. It can be expected that a higher concentration of amorphous forming solute would give more matrix into which oil globules can be incorporated and thus presumably a higher fraction of the lipid encapsulated.

In the study reported here, the distribution of oil between encapsulated and surface locations has been evaluated for a variety of freeze dried powders prepared from different solutes. For some of these support materials, the effect of oil phase volume on lipid distribution was also determined.

Materials and Methods

Preparation of Samples.

Oil-in-water emulsions were prepared with either triolein or linoleic acid. Solid supports which were present in the aqueous phase are listed below:

Support	Type	Source
Maltodextrin (DE = 15)	soluble carbohydrate	Grain Processing Co.
Maltose	soluble disaccharide	Fisher Chemical Co.
Carboxy methyl cellulose (CMC)	soluble cellulose gum	Hercules Chemical Co.
"Soluble" starch	polysaccharide	Merck
Avicel	microcrystalline cellulose	FMC Corp.
Gelatin	protein	Difco Labs
Egg Albumin	protein	Mann Research Labs
Glycine	crystallizing amino acid	Fisher
Urea	---	Calbiochem

Emulsifiers (Span 80 and Tween 80 at a 1:2 ratio) were used at a concentration of 9% of the oil phase. The emulsion systems were prepared by first blending the oil and Span 80 together, and then add-

ing this mixture to an aqueous solution or dispersion of the solute material and Tween 80. The emulsification was carried out by high speed mixing in a Sorvall Omnimixer for 10 minutes before adding the oil phase.

After emulsification the emulsions were transferred to trays, frozen at -20°C, then hard frozen at liquid nitrogen temperature (-196°C), and freeze dried as slabs of about 5 mm thickness.

Extraction of lipid phase.

Sequential extraction methods for quantitative evaluations of surface and encapsulated lipid were used. In the first step, a soxhlet extraction using hexane is carried out for 8 hours to remove surface fat from the freeze dried emulsions. (Microscopic observation of powder structure before and after this hexane extraction was used to insure that no changes in powder structure occurred. Potential structural transformations were avoided by operating the soxhlet at a low reflux rate). Residual hexane in the dry powder was removed by evacuation for about 1 hour. Surface oil extracted by the hexane was determined gravimetrically following vacuum evaporation of the hexane solvent and final drying at 50°C in a vacuum oven.

The extracted powder is then dispersed in water in a separatory funnel to disrupt the carbohydrate matrix and release the encapsulated

oil. Chloroform is added and the funnel is shaken. Ethanol is added to improve the sharpness of the interface between the water and the chloroform phases. The amount of the ethanol required depends on the concentration of oil, solids, water and chloroform. If desired, phase separation can be accelerated by holding the separatory funnel at 4°C for a few hours. The aqueous phase is re-extracted two times and the chloroform phases pooled. The oil present in the chloroform-ethanol solvent is also determined gravimetrically after vacuum evaporation of the solvent phase followed by drying overnight in a vacuum oven at 50°C. The total fat content of a freeze dried sample is also obtained using the water-chloroform-ethanol extraction. Total oil content determinations were in excellent agreement with the sum of the oil contents determined for the surface and encapsulated lipid fractions.

Microscopic Methods.

The various microscopic methods used have been described in detail by Gejl-Hansen and Flink (1976).

Optical microscopy (OM). Transmitted bright field microscopy was conducted on ground and flaked samples, immersed in either a drop of immersion oil (α - bromonaphthalene or paraffin oil) or, when the rehydrated condition was desired, in water as the immersion medium.

Surface deposits of fat in the freeze dried emulsions were visualized by staining the unsaturated bonds of freely available lipids (i.e. surface) with osmic acid vapors (Buchheim et al, 1974; Gejl-Hansen and Flink, 1976). The degree of darkening (light brown to black) depends on the surface oil concentration, degree of lipid unsaturation, and exposure time (usually 10 - 40 minutes). Microscopic observations showed that in cases where there was encapsulated oil it is protected by the impermeable matrix and does not react with the osmic acid vapors

Scanning Electron Microscopy (SEM). Small flakes of dried emulsion were attached to the aluminum SEM specimen holders with double sided adhesive tape or silver paint. The samples were then coated with a thin layer of aluminum or gold (approximately 100 - 400 Å) in a Bendix vacuum evaporator (Model CVC-14). A JEOL JSM-U3 scanning electron microscope was operated at 15 - 25 Kv. Secondary electrons were detected and used for image formation.

Electron Microprobe (EMP). The electron microprobe was used to detect surface oil in the osmium stained freeze dried oil-in-water emulsions. Following osmic acid treatment and OM observation, a coating with aluminum, and subsequent SEM observations, the coated samples are transferred to the electron microprobe and observed at an accelerating voltage of 15 Kv and a beam diameter of about 3 - 5 microns. Image formation is based on the intensity of the M_{α} X-ray line of os-

mium (λ = 6.49 Å) so osmium-rich areas (i.e. surface fat) appear as concentrations of bright dots on a dark background. Aluminum was used for coating since one of the M X-ray lines of gold interferes with the osmium signal. If desired the sample can be transferred back to the SEM or OM for further morphological studies.

RESULTS AND DISCUSSION

Effect of matrix forming solids on freeze dried emulsion structure.

Triolein emulsions were prepared using a variety of matrix forming solutes. The freeze dried materials were subjected to microscopic evaluations using OM, SEM, and EMP in combination with osmic acid staining. Table 1 summarizes the principal results.

Avicel:

Since Avicel is insoluble in water the homogenized dispersion contains oil globules together with rods and shredded pieces of cellulose crystals. Thus, emulsions containing microcrystalline cellulose (Avicel) as the solid support show a different type of emulsion structure than that observed with most other solutes examined. A typical sample contains oil globules in a size range of less than 1 micron to 8 microns and cellulose crystals anywhere from a few microns on the edge to a hundred microns. After freeze drying, microscopic examination shows the emulsion structure to be a dense network of cellulose crystals, but with no oil visible. In the SEM the characteristic wrinkled surfaces of the larger crystals is easily noted. This network structure of cellulose crystals is only obtained when the aqueous

dispersion has been mixed at high speed in the Omnimixer prior to addition of the oil phase. The shredding of the larger cellulose crystals produces smaller filaments, which have a bridging effect between the larger crystals resulting in a dense matrix structure. If this shredding step is omitted the freeze dried sample appears as the original free flowing powder. In the OM (Figure 1) the freeze dried emulsion shows the Avicel crystals, but again no oil is visible. Since amorphous cellulose material is not observed in either the OM or SEM, no oil could be encapsulated. Soxhlet extractions recovered all the oil (i.e. as free fat) (Table 2).

All the oil present was also isolated when the water-chloroform-ethanol extraction was used. Since neither method changes or disrupts the cellulose structure, all oil must be present as surface fat. Upon exposure to osmic acid vapors a strong reaction indicative of surface oil was obtained. Practically all surfaces are covered by oil due to the high fat concentration. It should be mentioned that pure Avicel does not react with osmic acid. Good EMP observations are not possible with Avicel systems because the curved surfaces of the micro-crystals cause the osmium X-ray signals from the fat deposits to be scattered and not caught by the detector, thereby preventing image formation.

Carboxymethyl Cellulose (CMC):

Fresh emulsions of CMC were made at a concentration of 0.5% w/w so that the viscosity of the aqueous solution would be similar to the other systems tested. Even with 1.15% w/w oil, the freeze dried emulsion showed only slight reaction with osmic acid, indicating that most of the oil phase is incorporated in the CMC matrix. This oil fraction is visible as a dense distribution of small oil globules in flexible plates of the solid CMC. In the EMP only scattered and weak signals were observed.

Figure 2 shows a SEM of the CMC emulsion. It was noted that areas of the platelet surface are quite rough, with small holes penetrating the surface. Using sequential OM, SEM and EMP techniques as described by Gejl-Hansen and Flink (1976), it was demonstrated that these holes gave pathways for contact of the "encapsulated" droplets with the environment. This contact probably accounts for the light OsO_4 staining and weak EMP signals.

Egg Albumin:

Fresh emulsion of egg albumin contained numerous oil droplets having an average size of less than 1 micron. The freeze dried structure consists of platelets with an abundance of tiny oil inclusions (Figure 3). These droplets are released upon addition of water to the dried matrix, and the oil size distribution is still less than

1 micron. This might be attributed to the emulsifying properties of the egg albumin itself. Exposure of the egg albumin emulsion to osmic acid gives spots of dark staining and additionally a uniform weak stain over the whole surface. However, the product is termed "non-sticky." The EMP for the egg albumin samples shows no locally stained areas, but rather a uniform weak signal intensity over the whole surface. This indicates that the staining reaction which took place was due not only to possible minor surface fat from the added oil but also to residual fat naturally present in the commercial egg albumin. A test showed that pure egg albumin will react somewhat with osmic acid.

Gelatin:

The freeze dried matrix of triolein and gelatin showed a very characteristic network structure. The smooth platelets that build up this network were observed to contain numerous tiny oil inclusions (Figure 4), which are only released very slowly in water as the matrix swells. The freeze dried emulsion is non-sticky and has no reaction with osmic acid, and no signal in the EMP. By microscopic analyses, it can be seen that gelatin was able to incorporate the oil, nearly quantitatively.

Glycine:

When fresh glycine-based emulsions, which contained well dispersed

1 micron oil droplets, were freeze dried, no oil is observed to be incorporated in the glycine phase. This is due to the fact that glycine does not form a concentrated amorphous phase during freezing, but rather a crystalline phase which totally excludes the oil droplets (Figure 5). In the freeze dried state surface oil never is observed as droplets since surface energy effects favor spreading of the oil. Exposure of the freeze dried glycine emulsion with its extensive surface oil to osmic acid gives a very dark staining reaction. The dried emulsion also has significant "stickiness." These facts indicate that the oil is present as a surface coating on the glycine crystals. Upon rehydration, the released oil globules are many times larger than the original 1 micron average diameter. The SEM shows the matrix to consist of thin needles and plates. No EMP image is observed since many needles are smaller than the probe diameter (1 - 3 microns) and the needle geometry sends emitted X-ray signals away from the detector.

Maltodextrin:

The freshly prepared emulsions had maximum oil droplet diameters of about 1 to 2 microns. The dried emulsion was noted to be very porous. In the optical microscope nearly all maltodextrin grains were smooth, with thicknesses averaging 8 - 12 microns. The grains contained spherical oil inclusions of diameters $\leq$ 10 microns (Fig-

ure 6). The relatively high content of surface oil was easily demonstrated by exposing dried grains to osmic acid vapors (Figures 7 and 8). It can be noted that concentrated staining occurred along surface characteristics (i.e. surface depressions due to ice dendrites, grooves, ridges, between platelets, etc.).

While rehydration gave a dispersion having globule diameters around 1 - 2 microns, a number of droplets having larger diameters (up to 35 microns) were observed. Rehydration of freeze dried emulsion which had its surface oil removed by the soxhlet extraction gave average globule sizes still around 1 - 2 microns, but no droplets were larger than 12 microns, the thickness of the maltodextrin plates.

Maltose:

Maltose-based emulsions showed different structural appearances which depended on the ability to conduct the freeze drying process without "collapse." "Collapse" is the viscous flow of the matrix which results from combinations of sample temperatures and moisture contents being above critical values (Bellows and King, 1972, 1973; MacKenzie, 1966; Tsourouflis et al, 1976). In the liquid state prior to freezing, the emulsion had an essentially uniform oil droplet size of about 1 micron, though a few larger droplets of up to 10 microns diameter were noted. The droplets were well dispersed, with no tendency to cluster.

When samples underwent partial collapse during freeze drying,

this could be observed macroscopically by the appearance of glossy areas, yellow areas (oil), and in some instances foam crusts. Under the optical microscope, oil inclusions, air inclusions, and holes were observed. Oil globules which were present in the fresh emulsion, but which were larger than the average grain thickness (9 microns) were not observed in the dry matrix. The appearance of many holes in the freeze dried maltose grains is an indication of the viscous flow (collapse) which occurred during freeze drying.

A typical grain structure for a maltose emulsion which freeze dried with collapse is shown in Figure 9 (exposed to osmic acid.) To be noted are the discontinuous staining areas, such as around the edge of hole (A), staining of "eggshell" area (B), and weaker staining at large depressions (C), which still include oil droplets in the bottom wall.

In the SEM the rounded form of the partially collapsed freeze dried emulsion, with its wrinkles, holes, and depressions, is noted (Figure 10). In the OM view of the grain (Figure 11) it is possible to see the rounded edges, the holes, and the unbroken large depressions ("eggshells") which appear lighter since they are much thinner (1 - 3 microns) than the rest of the grain, which is about 8 - 10 microns thick. It can be see that the walls of the "eggshells" contain oil inclusions. When freeze drying was conducted so that the

freeze dried cake showed no macroscopic areas of melting or collapse, the OM (Figure 12) showed a dense concentration of encapsulated globules. It is also noted that the grain structure was significantly different in appearance from that of the maltose emulsions which had undergone collapse: the edges of the grains were not rounded, but rather straight, and holes, depressions, and "eggshells" were very few in number. Exposure to osmic acid vapors showed surface fat as distinct, but discontinuous deposits, generally of much smaller size than the large pools of surface fat encountered for the collapsed emulsion sample. The rehydrated emulsion shows most oil globules to be larger than present in the original, which was less than 1 micron to 2 microns. Many oil globules have diameters ranging from 10 to 30 microns.

Starch:

Emulsions of "soluble" starch were freeze dried and observed for lipid location. Upon microscopic examination, the matrix was found to consist of clusters of intact starch granules with no visible amorphous phase, indicating that the starch had not been heated sufficiently to be gelatinized during preparation. No oil was incorporated in the starch granules; no droplets were visible. However, the very sticky matrix reacted strongly with osmic acid and SEM (Figure 13) showed oil bridges between granules at locations which would give

especially dark staining. It was also noted that large lenses of oil would appear upon addition of water. This indicates that the fat is present as a surface layer on the granule. No EMP image could be obtained since the sperical fat-coated granules do not give good directional reflection of the X-rays towards the detector.

Urea:

The specific interaction of urea with certain lipid materials when prepared from solution is well known (Martinez Moreno and Vasquez Roncero, 1964). There is one report that in a urea-based freeze dried emulsion the lipid phase was present as discrete droplets external to the crystalline urea needles (Lladser et al, 1968). Urea samples were therefore prepared by precipitation from saturated methanol solutions and by freeze drying of aqueous emulsified systems.

Samples were prepared by adding the following lipid materials to a methanol solution saturated with urea: a) no lipid present, b) triolein and c) linoleic acid. The oil concentration was about 3% of the urea-methanol solution (which had been decanted from the saturated solution so that no undissolved urea was present). No precipitation of urea was noted in the lipid-free samples, unless some of the methanol was evaporated. Triolein is not solubilized by the methanol and thus was present on the bottom of the flask as distinct oil globules around which there was a slow precipitation of urea during a 24 hour

period. In the linoleic acid sample, precipitation was rapid, occurring within a minute.

Microscopic investigation of the urea crystals recovered from the methanol solutions showed a distinct difference in the crystal morphology. The pure urea formed short rods while the oil-containing urea samples appeared as long slender needles with visible oil inclusions. These observations show that linoleic acid, and, to a lesser extent, triolein, form urea adducts which have a needle-like morphology.

Urea freeze dries to give a crystalline solid in the form of clusters of short rods or needles. The morphological pattern of the urea crystals is constrained by the limited growth space in the eutectic caused by the already formed ice crystals. Therefore comparisons of the crystal morphology of these freeze dried samples with the above mentioned oil-urea-methanol systems should be done very cautiously.

When aqueous solutions of urea (20% w/w) containing triolein (1%, 3%, 5% w/w) were freeze dried, small oil droplets (diameters $\leq$ 1 micron) were observed to be trapped within the crystalline structure. These oil droplets were not dissolved when the freeze dried urea samples were subjected to the hexane extraction. Addition of water gave solution of the urea crystals, resulting in the appearance of large numbers of oil droplets having a wider range of diameters (up to 10

microns) than has been observed in the dried systems. When exposed to osmic acid vapors, the freeze dried triolein-urea systems turn dark, with samples having higher oil phase volumes giving stronger reaction. Samples washed in hexane (which did not change the matrix structure) did not react with the osmic acid. These facts, together with the observed stickiness of the dry particles suggests that oil is also present on the surface.

Freeze dried samples of urea (20%) and linoleic acid (1%, 5%) show very much the same morphological patterns as mentioned above for triolein-urea emulsions. The urea forms needle-like structures with lipid inclusions generally 1 to 2 microns in diameter (Fig. 14). It appeared that the linoleic acid systems contained fewer visible droplets than the corresponding triolein systems which is not surprising considering its potential for adduct formation. Upon exposure to osmic acid vapors the 1% linoleic acid sample show no staining, indicating that all the oil was present in the adduct. The 5% linoleic acid sample showed little or no staining upon prolonged exposure to osmic acid indicating that the urea (20%) was still able to encapsulate practically all the oil, leaving essentially none as free surface fat.

When freeze dried urea-linoleic acid samples, or hexane-washed urea-triolein samples (i.e. surface oil removed) were rehydrated, oil globules with diameters much larger than observed in the dried sample

were noted. Droplet diameters up to 12 microns were not unusual. In this case the mechanism of dissolution of the urea crystals results in the occluded lipid being released under conditions which foster potential coalescence, thus giving the observed increase in maximum droplet size.

Influence of Oil-Solid Ratio on Degree of Encapsulation in Freeze Dried Emulsions

Maltodextrin emulsions (20% w/w solids) containing triolein at 0.5 to 10% w/w levels were quantitatively evaluated for oil distribution by Soxhlet hexane extraction (surface fat) and water-chloroform-ethanol extraction (encapsulated fat). Optical microscopy showed that density of inclusions in the matrix was increasing with increasing oil concentration, though the samples appeared similar for oil concentrations above 1%. Similar observations were found for linoleic acid based emulsions. The amount of fat encapsulated in the maltodextrin was found to increase with oil concentration (Table 2). Table 2 also shows that for the range of triolein:maltodextrin ratios examined, the encapsulated oil was about 10% of the total oil present in the system. This is significant since it indicates that while 100% encapsulation was never observed, even at low oil concentrations (0.05 gram oil per gram maltodextrin), emulsion samples could be prepared with an amount of oil encapsulated which was greater than the total amount of oil present in the low oil

concentration systems. For example, while the emulsion containing 0.51 gram oil per gram maltodextrin has an amount encapsulated (0.056 gram oil per gram maltodextrin) which is higher than the total amount of oil present in the 0.026 gram oil per gram maltodextrin emulsion, only 8% of the latter emulsion's oil was encapsulated.

Quantitative Measures of Lipid Distribution

Table 3 gives quantitative measures of the distribution of lipid (triolein or linoleic acid) for systems of maltodextrin, Avicel or maltose. For three of the maltodextrin samples the influence of initial lipid phase volume on the amount encapsulated is similar to that noted in Table 2. These three samples have a high surface oil concentration, in agreement with the information presented in Table 1 for maltodextrin emulsions.

On one occasion, however, a maltodextrin-linoleic acid emulsion at a high lipid phase volume (5.5% w/w) gave a high degree of encapsulation as measured by the hexane Soxhlet extraction. The high degree of encapsulation was confirmed by optical microscopy. Very dense concentrations of deformed oil globules were observed in practically all maltodextrin grains (Fig. 15). It should be noted that these oil inclusions are present as individual droplets, and not as undefined discontinuities. The majority of the grains appeared flat and smooth (also confirmed by SEM). Exposure of dried grains to osmic acid gave only

scattered darkening, with the staining generally associated with areas having a rough surface topology, such as ridges, depressions, groves and closely spaced parallel flakes. The EMP showed signs of low intensity only along these topological features, confirming low surface fat concentrations.

This high degree of encapsulation could not be repeated in several subsequent attempts, and it is not known what particular factors resulted in the high encapsulation this one time. Evaluations using maltodextrins of other DE values, on the chance that a formulation error was made failed to yield a high level of encapsulation. It can be speculated on the basis of observations made that some change in the emulsifier system resulted in an emulsified system which was more stable to freezing drying stresses than the usual system. While not a conclusive indication that the emulsifier is responsible, it is interesting that the "droplets" can be stabilized as individual units with such extensive geometric deformation. It is also interesting that contrary to behavior noted earlier for samples showing distorted droplets (Gejl-Hausen and Flink, 1976), the surfaces of platelets of this emulsion show no holes due to penetration of droplets.

The Avicel systems show that 100% of the oil is present as a surface layer, which agrees with all the powder characteristics noted above.

As noted above, freeze dried maltose samples were obtained with or without collapse occurring. These samples were found to have

different extents of oil encapsulated, with collapse resulting in an increase of surface oil (Table 3). This results since collapse is the phenomena of viscous flow of the matrix. In the process of drying, if the matrix conditions are such that the matrix is somewhat plastic, then vapor formed in the matrix can deform the maltose matrix elements giving rise to expanding films. If the vapor expands sufficiently so that it breaks through both sides of the maltose phase, holes will be formed, while if one film yields first, a large depression with a thin bottom results (Fig. 11). When this flow of the maltose matrix occurs, the encapsulated droplets are subjected to shear stresses which deform them from their spherical shape, which together with the formation of new surface and matrix elements of decreased thickness results in localized breakthrough and spreading of the formerly encapsulated oil phase. The fact that collapse has occurred does not mean that spillage of encapsulated oil must occur. Thus, while heavy OsO_4 staining occurs at the edges of holes and the thin films in the bottoms of the large depressions are lightly stained, there are some encapsulated droplets remaining in the thin films, and much of the matrix shows numerous encapsulated droplets (Fig. 9).

CONCLUSION

The above results show how the fate of the oil phase is dependent on whether it can be incorporated in an amorphous solute (egg albumin, gelatin, CMC) during freezing or excluded when the matrix forming solute is an insoluble crystalline solid (starch) or crystallizes as water is removed from the solution (glycine). The results show that a macroscopic observation termed "stickiness" correlates qualitatively very well with osmic acid staining as seen in the OM. Furthermore, the darkness of the osmic acid staining was found to correlate very well with EMP image strength except in the case of adverse matrix structure geometries (glycine and starch).

It was noted that levels of encapsulation never reached 100%, even if at low phase volumes of oil, such that the total amount of oil present was much less than the amount which could be encapsulated by the matrix-forming solute, if it had been freeze dried from an emulsion with a higher phase volume of oil.

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Table I

MICROSCOPIC EVALUATION OF FREEZE DRIED TRIOLEIN EMULSIONS

	total % oil on dry basis	matrix structure	incorporated oil droplets	droplets upon rehydration	sticky surface	(Stain	
Avicel	23	micro-crystals	none	yes, large	yes	very dark	none
CMC	70	flexible plates not smooth (SEM)	many small	some	no	light	weak
egg albumin	20	flaky platelets	numerous tiny	yes	no	dark	weak
gelatin	33	hard honeycombed network	many tiny	matrix swells slow release	no	white	none
glycine	20	anisotropic plates needles	no	yes, many large	very	very black	none
maltodextrin	20	plates	many	yes, many	yes	dark	strong
maltose	20	plates	many	yes, many	yes	dark	strong
starch	20	intact granules	none	many large appear	very	very dark	none
urea	20	needles	small only	many, also large	yes	very dark	none

Table 2

EFFECT OF TRIOLEIN PHASE VOLUME ON
NCAPSULATION FOLLOWING FREEZE DRYING

Emulsion Composition[a]		Oil Encapsulated	
g oil / g maltodextrin	% (w/w) of oil in fresh emulsion	g oil / g maltodextrin	% of total oil
0.026	0.51	0.002	8
0.053	1.05	0.004	8
0.130	2.60	0.013	10
0.250	5.00	0.021	8
0.510	10.21	0.056	11

a) All fresh emulsions contained 20% (w/w) maltodextrin.

Table 3

LIPID DISTRIBUTION IN FREEZE DRIED EMULSIONS

Emulsion[a] Composition	g oil / 100 g dry emulsion	Surface[b] Oil	Encapsulated[b] Oil	g oil encapsulated / g carbohydrate
1.1% linoleic acid 20% maltodextrin	5.2	79	21	0.012
5.5% linoleic acid 20% maltodextrin	21.6	26	74	0.204
2.0% triolein 20% maltodextrin	9.1	80	20	0.020
5.1% triolein 20% maltodextrin	20.3	90	10	0.026
0.75% linoleic acid 15% Avicel	4.8	100	0	0
4.5% linoleic acid 15% Avicel	23.1	100	0	0
3.75% linoleic acid 15% maltose	20.0	88	12	0.030
3.75% linoleic acid[c] 15% maltose	20.0	97	3	0.008

a) Concentrations in (w/w).
b) Percentage of Total Oil.
c) Collapsed during freeze drying.

LIST OF FIGURES

Figure 9. Optical microscope view of 3.75% linoleic acid, 15% maltose freeze dried emulsion (collapsed), exposed to OsO_4 vapors (600X).

A) hole

B) "eggshell"

C) depression with thin bottom

Figure 10. Scanning electron microscope view of 3.75% linoleic acid, 15% maltose freeze dried emulsion (collapsed) (coated with aluminum) (320X).

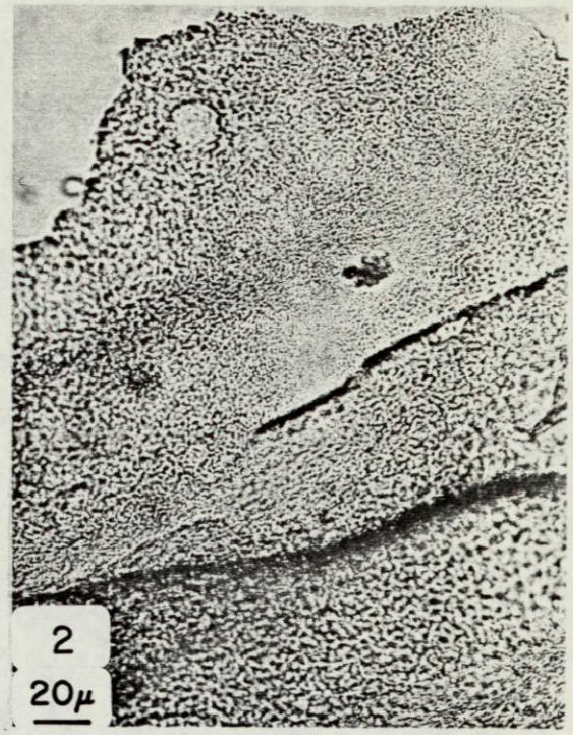
Figure 11. Optical microscope view of same field as in Fig. 9 (400X).

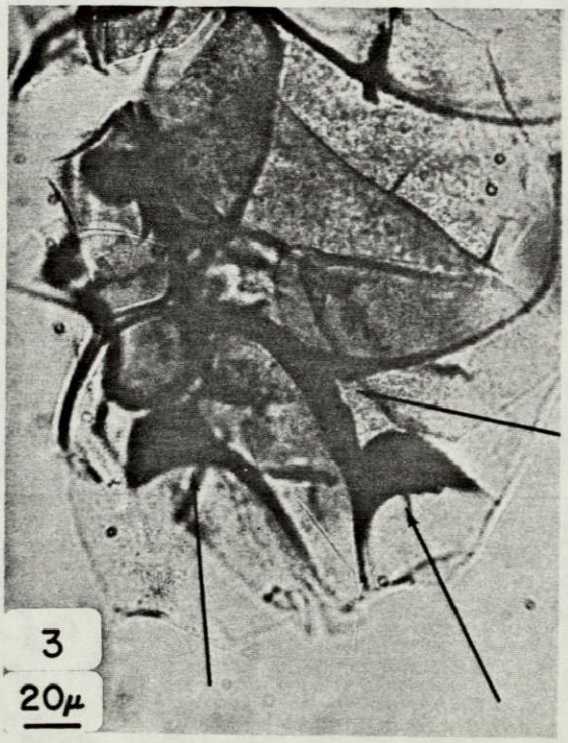
Figure 12. Optical microscope view of 3.75% linoleic acid, 15% maltose freeze dried emulsion (non-collapsed) (150X).

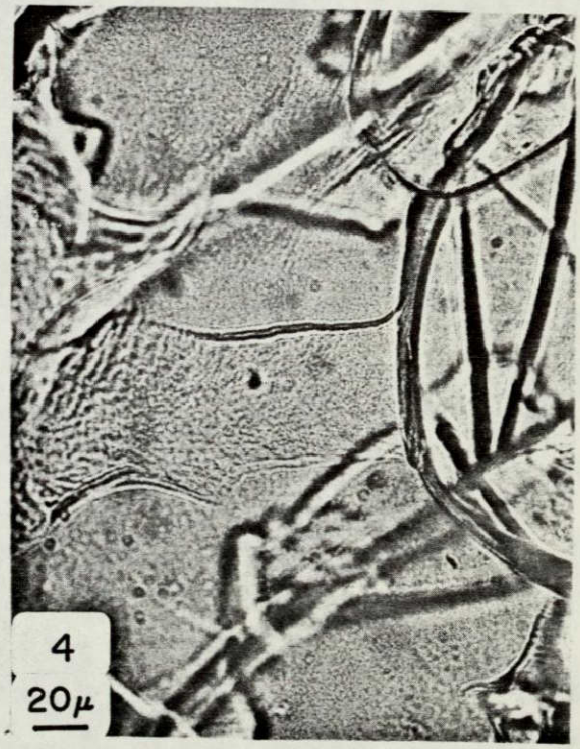
Figure 13. Scanning electron microscope view of 5% linoleic acid, 20% starch freeze dried emulsion, exposed to OsO_4 (coated with aluminum) (1500X).

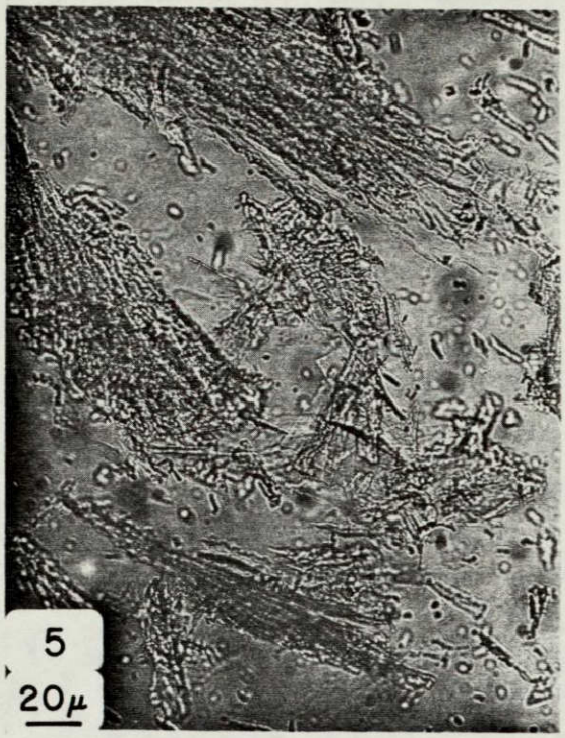
Figure 14. Optical microscope view of 5% linoleic acid, 20% urea freeze dried emulsion (400X).

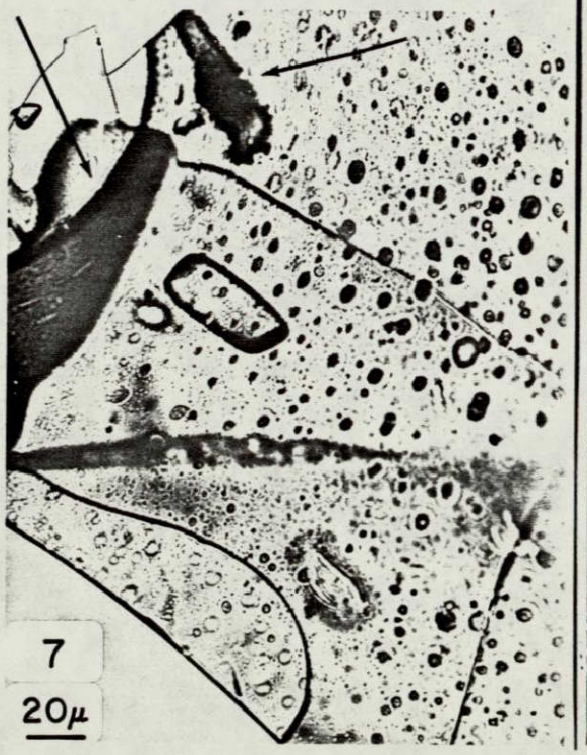
Figure 15. Optical microscope view of 5.5% linoleic acid, 20% maltodextrin freeze dried emulsion (400X).

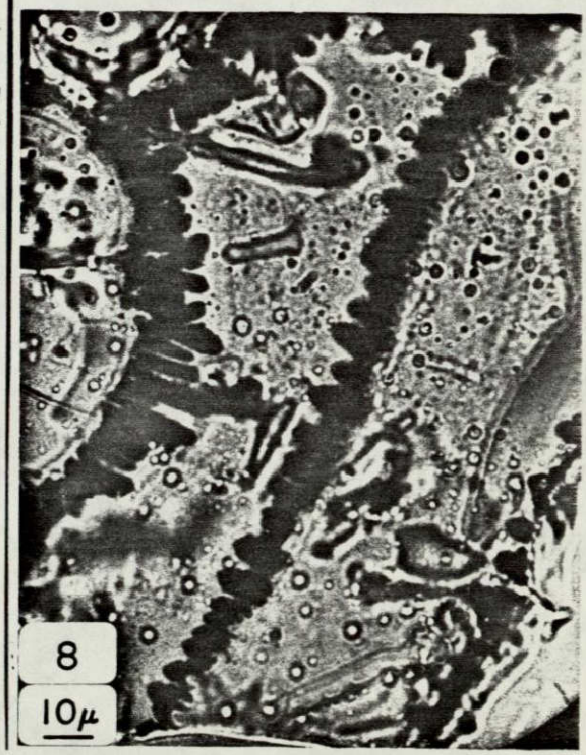


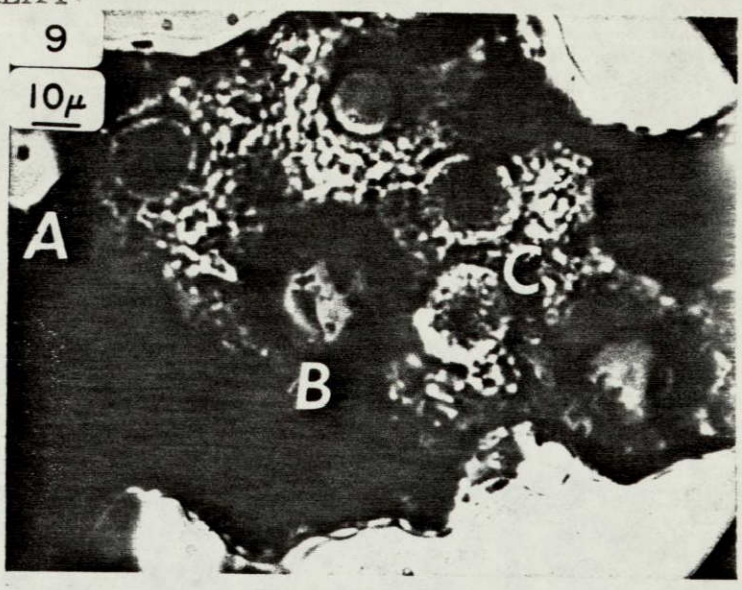


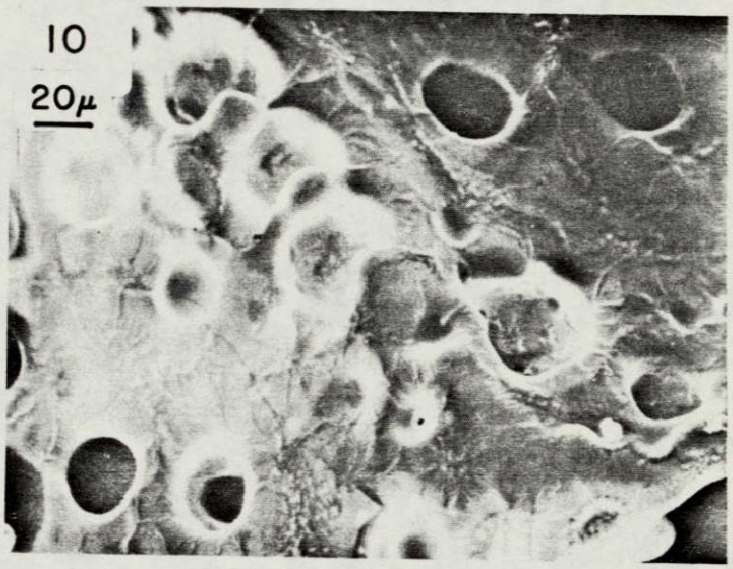


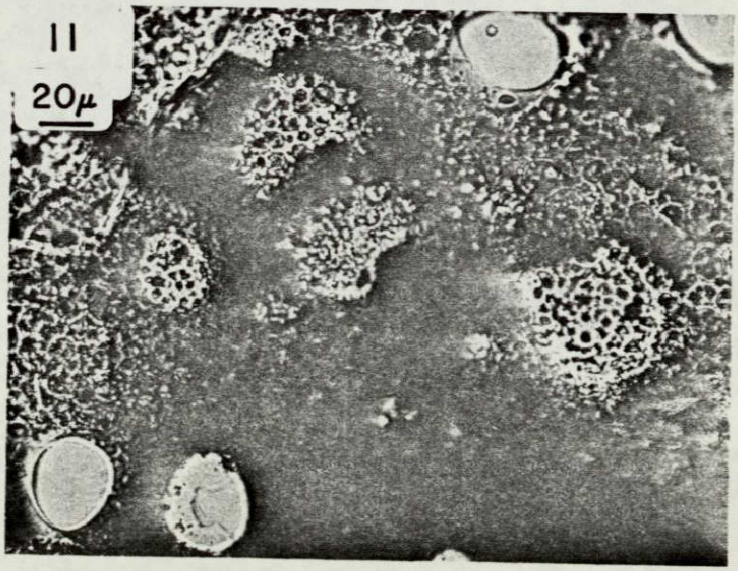


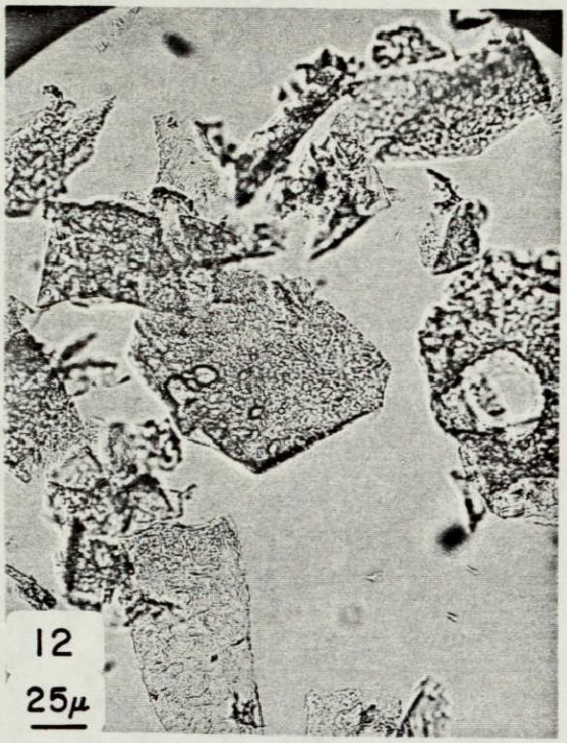












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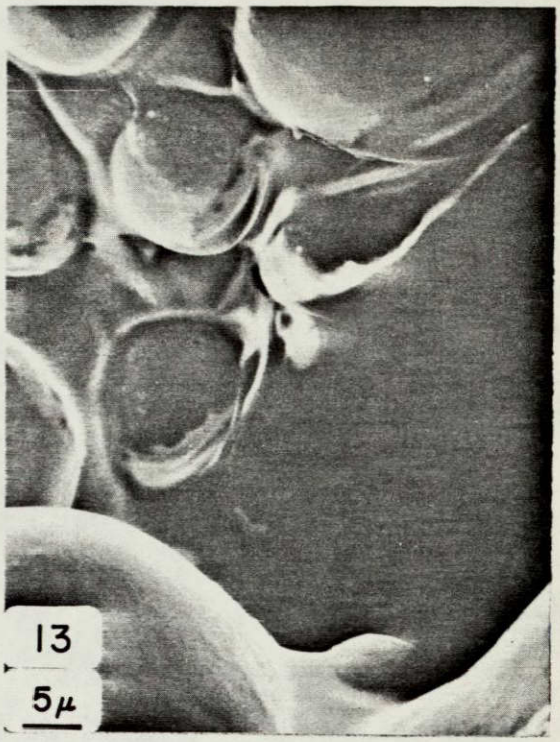

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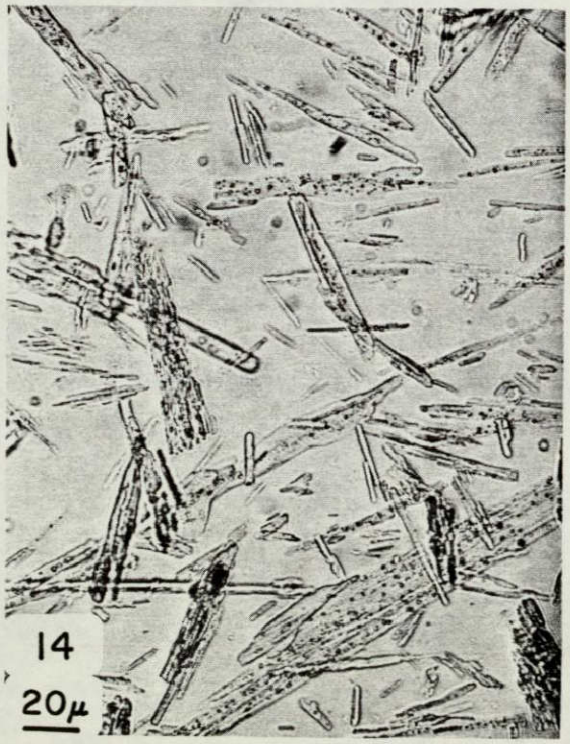

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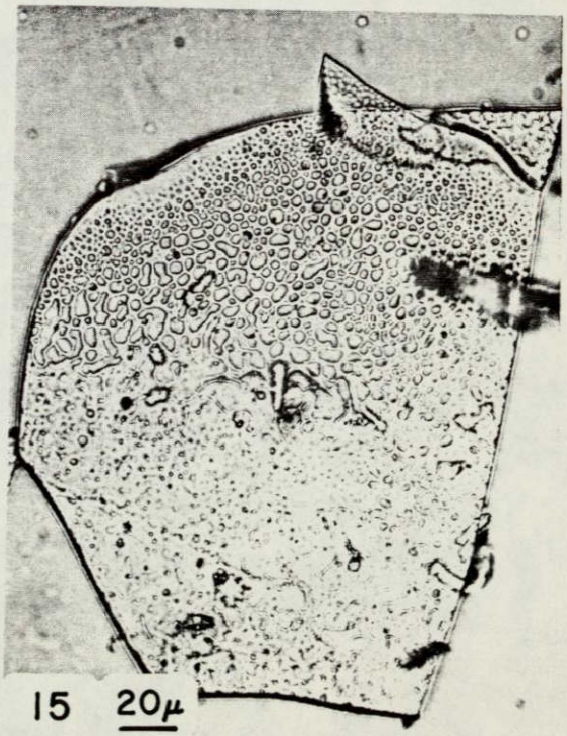

15 20μ

3. Investigations of Structural Changes in Freeze-dried Systems

Work described in the Phase IV final report was published in the Journal of the Science of Food and Agriculture (J. Sci. Fd. Agric. 27:509-519). A reprint of that scientific paper is presented here.

J. Sci. Fd Agric. 1976, **27**, 509–519

Loss of Structure in Freeze-dried Carbohydrates Solutions: Effect of Temperature, Moisture Content and Composition

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During processing and storage, dehydrated food materials are subject to changes in their structure. Terms used to describe these changes, which are due to the same basic phenomena, vary from process to process. Thus, during freeze-drying, loss of structure is called "collapse", while during storage, phenomena related to viscous flow of the dried powder matrix are termed "stickiness". This loss of initial structure often results in the loss of desirable product qualities, though in some cases controlled manipulation of these changes is used to produce improved products. In freeze-drying, collapse of capillaries in the dry layer results in puffing and loss of desirable structure. In dehydrated powders "stickiness" leading to caking and other defects is also a result of collapse phenomena. The collapse temperature of freeze-dried orange juice and carbohydrate solutions was investigated as a function of moisture content and sample composition. It was observed that collapse temperatures decreased as the sample moisture content increased. Mixtures of materials collapsed at a temperature intermediate to that of the individual components. The consequences of these observations to a number of food processes are discussed.

1. Introduction

Changes in structure (macroscopic or microscopic) of dehydrated materials in response to environmental stresses have been reported in the literature for a number of situations. While it appears that these structural changes are manifestations of the same basic phenomena (time, temperature and moisture dependent viscous flow), a variety of expressions which describe sensory behaviour of the materials are used in the literature. (Throughout this paper we will use the term "collapse", which has been used to characterise loss of structure during freeze-drying.)

It is noted in the literature that some products undergo "collapse" during freeze-drying when the frozen sample temperature is higher than some characteristic temperature, called the collapse temperature (T_c). For various aqueous solutions, collapse temperatures vary over a wide range, from -5 to -60°C.[1–3] A collapsed product loses its shape by becoming a highly viscous liquid and often shows poor aroma retention, poor rehydration characteristics and uneven dryness. When collapse occurs during freeze-drying, ice crystals appear to dissolve rather than to sublime, resulting in obliteration of capillaries and thus an increased vapour flow resistance. Extreme collapse completely closes the capillaries, so that moisture removal is limited to evaporative mechanisms, with much bubbling and spattering.[1,2]

A number of cases of structure transformation from dried products to the viscous state due to added moisture and/or increased temperature are of importance in industrial practice. Concentrated liquid foods such as tomato juice and concentrated orange juice often show problems during spray-drying due to "stickiness" of the drying particles. Scorching of particles sticking to the walls of dryers, and difficulties in collecting powder in the collecting zones are a consequence of this stickiness. The "sticky-point" temperature marks a transition from a stable dry powder to a viscous state and is thus related to collapse.[4,5]

Instantising of powders by "agglomeration" is also related to collapse. This process depends on controlled raising of the moisture content of surfaces of powder to a level which makes these surfaces sticky at the desired temperature. The wetting is conducted under conditions which result in the particles sticking together in clusters, which are then dried to the desired moisture content.[6]

"Caking" of foods during storage is also related to collapse. Pisecky[7] observes that when sufficient moisture is present, sintering of dried particles can occur, which results in the loss of the powder character for the material. Again, the moisture and temperature dependent transformation to the viscous liquid is responsible for this physical change.

During storage, optimum moisture and temperature conditions must be maintained to avoid structural change of the material and the resultant loss of desirable product properties. For the design of spray-drying or agglomeration processes, it is necessary to understand the dependence of "sticky-point" temperatures on moisture contents.

Recently, theories have been developed to explain collapse phenomena occurring during freeze-drying. One of these theories, the Amorphous Viscosity Theory,[8] appears to be utilisable to describe collapse phenomena in general, if it is remembered that particular critical values of environmental parameters will be very different for the different situations considered.

The explanation of collapse phenomena occurring during freeze-drying is based on phase transition phenomena which occur during the initial step of freezing. During freezing, most compounds of interest in foods, such as sugars for example, do not nucleate and formation of solid eutectic mixtures does not occur; rather the solution becomes more concentrated as water is transferred to ice crystals. According to MacKenzie[2] and White and Cakebread,[9] at sufficiently high solute concentration, which during freezing coincides with attainment of low temperatures, the remaining solution will undergo a glass transition and no more ice is formed. The Amorphous Viscosity Theory of Collapse considers the matrix as a concentrated amorphous aqueous solution. As long as the temperature of the solute matrix is below some critical value, the collapse temperature, the matrix is sufficiently viscous to behave like a solid. This viscosity is related to the combination of solids content (i.e. moisture content) and temperature, which for the case of the frozen material, are both related to temperature. If the temperature of the frozen zone rises above the collapse temperature, the concentrated amorphous solution becomes less viscous because of dilution with water due to ice melting, as well as because of the direct effect of temperature on viscosity.[1] As water is removed during the drying, the matrix becomes more rigid and can tolerate higher temperatures without undergoing viscous flow.

As noted in the description of *stickiness* etc. above, the phenomena associated with changes in the structure of "dry" materials are also related to combined temperature and moisture stresses, just as is indicated in the Amorphous Viscosity Theory of Collapse.

We have studied collapse phenomena of freeze-dried carbohydrates and of orange juice as a function of moisture and temperature. The use of additives to raise the collapse temperature or to increase the moisture content at which collapse occurs at a given temperature was also studied.

2. Experimental

Systems studied included orange juice, with or without addition of various carbohydrates, and solutions of several carbohydrates. Commercial frozen concentrated orange juice was used and was reconstituted according to manufacturer's instruction. The sources of the carbohydrates used are shown in Table 1.

Solutions of the carbohydrates in water or in the orange juice were prepared in the desired concentrations, and 2 ml aliquots were delivered with a syringe to preweighed 5 ml ampules. The samples were then frozen with the ampules in a tilted position so that a greater surface area could be obtained. This improved the rate of the subsequent freeze-drying and humidification steps and also aided the visual determination of collapse. The samples were either slowly frozen (overnight at 0°F (−18°C)) or rapidly frozen in liquid nitrogen. Following freezing, the samples were freeze-dried for 48 h. The weight of freeze-dried solids was determined for each sample.

Table 1. Carbohydrates used in the study

Carbohydrate	Grade or type	Source
Lactose	D(+)-Lactose, monohydrate powder, reagent	J. T. Baker Chemical Co., Phillipsburg, NJ
Maltose	Powder, reagent	Fisher Scientific Co., Fairlawn, NJ
Sucrose	Crystals, reagent	MCB, Norwood, Ohio
Maltrin-100	Maltrodextrin, Ave. DE = 10	Grain Processing Co., Muscatine, Iowa
Maltrin-150	Maltrodextrin, Ave. DE = 15	Grain Processing Co., Muscatine, Iowa
Maltrin-200	Maltrodextrin, Ave. DE = 20	Grain Processing Co., Muscatine, Iowa
Maltrin-250	Maltrodextrin, Ave. DE = 25	Grain Processing Co., Muscatine, Iowa
Starch	Soluble starch, reagent	Merck and Co., Inc., Rahway, NJ
Gum arabic	A-12	Stein, Hall and Co., New York, NY
Locust beam gum	175 mesh	Stein, Hall and Co., New York, NY
Tragacanth gum	Powder, T-500	Stein, Hall and Co., New York, NY
Karaya gum	Powder, K-1	Stein, Hall and Co., New York, NY
Tapioca dextrin	Powder, K-Dex 4484	Stein, Hall and Co., New York, NY

The samples were then humidified to different moisture contents ranging from about 0–10%. In a typical experiment, seven to eight samples of different moisture content were used. The humidification was conducted at 32°F (0°C) to avoid collapse during sample conditioning. Samples were humidified by either holding for different lengths of time in an evacuated desiccator containing a saturated solution of K_2SO_4, maintaining a constant relative humidity of 97%, or by holding the samples for a fixed time period over a series of constant humidity solutions ranging from 11% RH (LiCl) to 97% RH (K_2SO_4).

After humidification, the ampules were carried in ice to the analytical balance, where the water pick up was determined gravimetrically. Moisture uptake is expressed as per cent of total weight of dry solids in the ampule. Freeze-dried samples were defined as free of water and all subsequent uptakes are relative to this zero basis. Immediately after weighing, the neck of the ampule was flame-sealed while the body of the ampule was kept cool by holding it in a chilled wet cloth.

For determination of collapse temperature, two identical water-baths were used to evaluate the temperature of the samples in 10°F (5.5°C) increments. While the samples were being held at a constant temperature in one of the water baths, the other was equilibrating to the next desired temperature (10°F (5.5°C)) higher. The elevation of temperature was continued until all samples had collapsed or until the maximum temperature of the bath was reached (210°F (99°C)). An oil bath or an oven was used for temperatures above 210°F (99°C). Collapse was observed visually and was defined as the change of the appearance of the sample's surface. The collapsed sample resembles a highly viscous, glassy material compared to the pre-collapse appearance which is that of a porous solid. It is to be expected that for a dynamic phenomenon involving flow of viscoelastic materials, the evaluation of collapse will depend on the length of time allowed for observation.[10] At a given moisture, the *rate* of the transformation step will vary with temperature so that, for a given extent of transformation (i.e. the not collapsed/collapsed boundary) the collapse temperature determined will depend on the time period used. A preliminary test showed that for our system, the time required for collapse varied with holding temperature as shown in Figure 1. The converse of this observation means that for holding times over 45 min, the collapse temperature remains relatively constant at its lowest value for a given moisture content. For this reason, samples were held 45 min at each temperature for the determination of collapse. If collapse occurred *prior* to the end of this holding period, the collapse temperature was estimated by an interpolation which assumed that a linear relation between collapse temperature and time within the narrow specified limits (time interval = 45 min; temperature interval = 10°F (5.5°C)) was a sufficiently accurate model of the expected more complex exponential behaviour.

Thus the estimated collapse temperature (T_c) was obtained by using equation (1):

$$T_c = T_B - \left(\frac{t_c}{45}\right)(10°\text{F}) \qquad (1)$$

where T_B = Bath temperature (°F) and t_c = time in minutes to collapse following the transfer to bath maintained at T_B from bath maintained at $T_B - 10$°F.

3. Results

Collapse temperatures for several of the systems studied are presented in Table 2. These temperatures were obtained on materials in dry state. Collapse temperature dependence on moisture content was also studied in a number of systems. Figure 2 shows the moisture content dependence of the

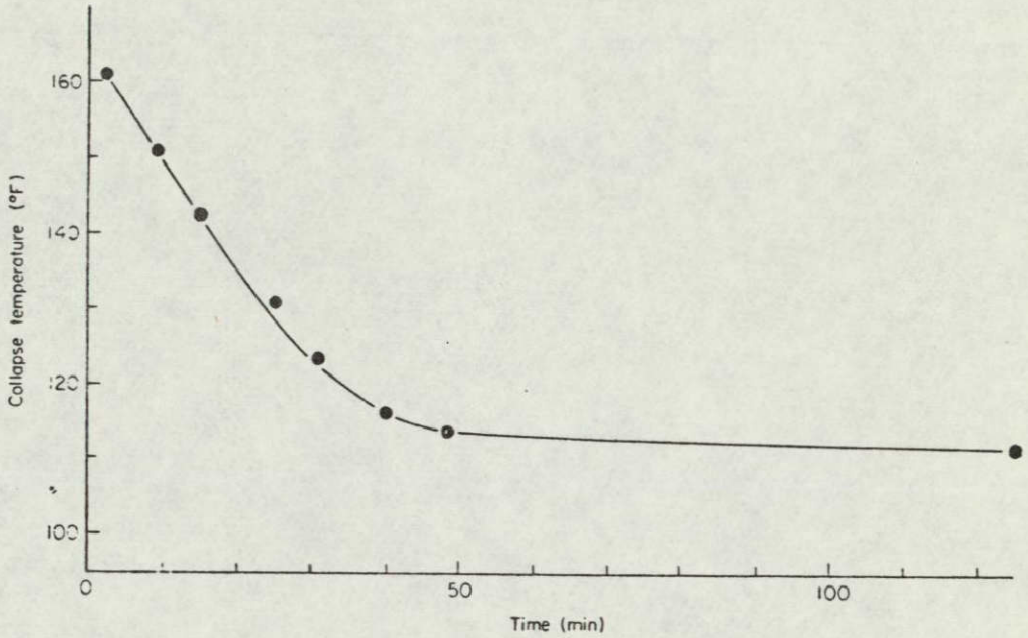

Figure 1. Time required for collapse when holding dry sucrose at specified temperatures. (Sucrose freeze-dried from 25% solution, fast freezing was used).

collapse temperature for maltose. The collapse temperature of dry maltose is high: 205°F (96°C). The mode of freezing has only a slight effect on the collapse temperature of the rehumidified freeze-dried material. For maltose, the slowly frozen samples show a slightly higher collapse temperature at all moistures than the fast frozen samples. In experiments with lactose, we observed a reverse behaviour with slowly frozen samples having a slightly lower T_c.

The dependence of T_c on moisture content in a mixture of sucrose and maltose is shown in Figure 3. The data are typical of those obtained with binary mixtures of sugars. The collapse temperature of the mixtures are typically intermediate between the temperatures for the two individual components.

The maltodextrins used in this experiment (Maltrins: M-100, M-150, M-200, M-250) all have a high collapse temperature (Figure 4). The collapse temperature is a function of the dextrose equivalent (DE) of the maltodextrin. Maltrins with higher DE, that is, with a lower average molecular weight, show a lower collapse temperature (M-250 at 400°F (204°C)) while Maltrins with lower DE (higher average molecular weight) have a higher collapse temperature (M-100 at 480°F (249°C)). Maltrins with intermediate DE collapse at intermediate temperatures. The rate of freezing was not found to have any effect on the collapse temperature of Maltrins.

As shown in Figure 5, the collapse temperature of pure orange juice is relatively low, the dry juice collapsing at 125°F (52°C). This collapse temperature is very close to that of sucrose (132°F (55°C)) which is not unexpected since orange juice has a high content of sucrose. According to Bellows,[8] 50% of the sugar present in orange juice is sucrose.

Table 2. Collapse temperatures of freeze-dried systems[a]

System	mol. wt	Viscosity (cP)	T_c (°F)
Lactose, 25% w/v	342	2.2	214
Maltose, 25% w/v	342	2.2	205
Sucrose, 25% w/v	342	2.2	132
Sucrose–lactose, 12.5–12.5%	342	2.0	174
Sucrose–maltose, 12.5–12.5%	342	2.1	164
Maltrin-100, 25%[b]	1710	6.2	480
Maltrin-150, 25%	1140	3.4	450
Maltrin-200, 25%	855	3.3	450
Maltrin-250, 25%	684	3.1	400
Orange juice, 14.2% w/v	277	4.0	125
Orange juice + 10% maltose	283	4.8	150
Orange juice + 2% starch	—	4.1	128
Sucrose + 2% starch	—	2.3	164
Orange juice + 3% M-100	320	5.1	167
Orange juice + 5% M-100	349	5.4	173
Orange juice + 10% M-100	420	7.1	183
Orange juice + 15% M-100	492	8.3	192
Orange juice + 20% M-100	564	11.6	212
Orange juice + 2.5% M-250	287	4.7	137
Orange juice + 5% M-250	297	5.4	145
Orange juice + 10% M-250	317	6.7	155
Orange juice + 15% M-250	338	7.1	164
Orange juice + 20% M-250	358	9.3	183
Orange juice + 1% gum arabic	—	6.5	135
Orange juice + 3% gum arabic	—	12	142
Orange juice + 6% gum arabic	—	13	180
Orange juice + 3% locust bean gum	—	1060	212
Orange juice + 3% tragacanth gum	—	>2000	210
Orange juice + 3% karaya gum	—	>2000	152
Orange juice + 3% tapioca dextrin	—	7.4	152
Orange juice + 6% tapioca dextrin	—	8.0	153
Orange juice + 10% tapioca dextrin	—	9.9	174

[a] All concentration and viscosity data refer to solutions prior to freeze-drying. The T_c is for systems in the dry state.

[b] Molecular weights of all Maltrins are based on oligosaccharide distribution data supplied by manufacturers.

In this case, freezing rate has relatively little influence on collapse temperature. The low collapse temperature observed for the freeze-dried orange juice is directly associated with the difficulties encountered in preparing the dried material. During the initial steps of freeze-drying, there is some melting and puffing; however, there is sufficient unpuffed material to allow determination of the collapse temperature.

Four Maltrins (M-100, M-150, M-200 and M-250) were added to orange juice at different concentrations and the change of collapse temperature with Maltrin concentration was studied. Collapse was studied only at 0% moisture. As Figure 6 shows, there is a considerable effect of added maltodextrins on the collapse temperature of dry juice. It can also be seen that the collapse temperature changes with average molecular weight of the Maltrins. Low DE Maltrins give higher collapse temperatures for the orange juice mixture than high DE Maltrins at the same concentration.

Figure 7 shows the increase in collapse temperature of orange juice with increasing concentration of gum arabic, again only for 0% moisture samples. There is a considerable increase in collapse temperature and it is affected by the mode of freezing.

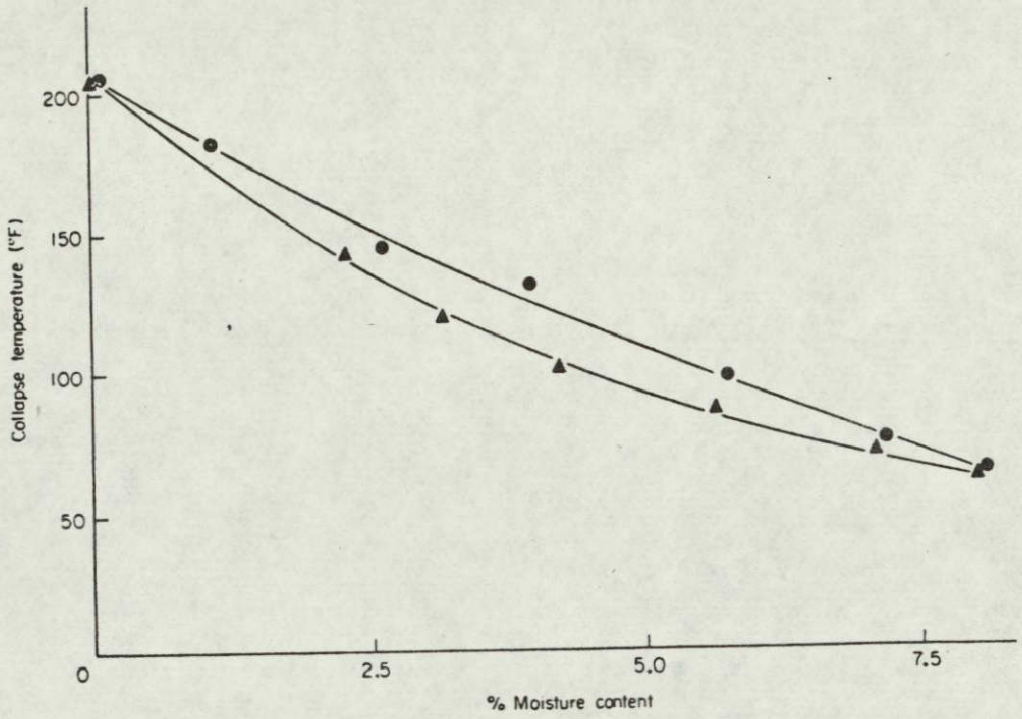

Figure 2. Collapse temperature *vs* moisture content for maltose (25% solids, fast and slow freezing). ▲, Fast freezing; ●, slow freezing.

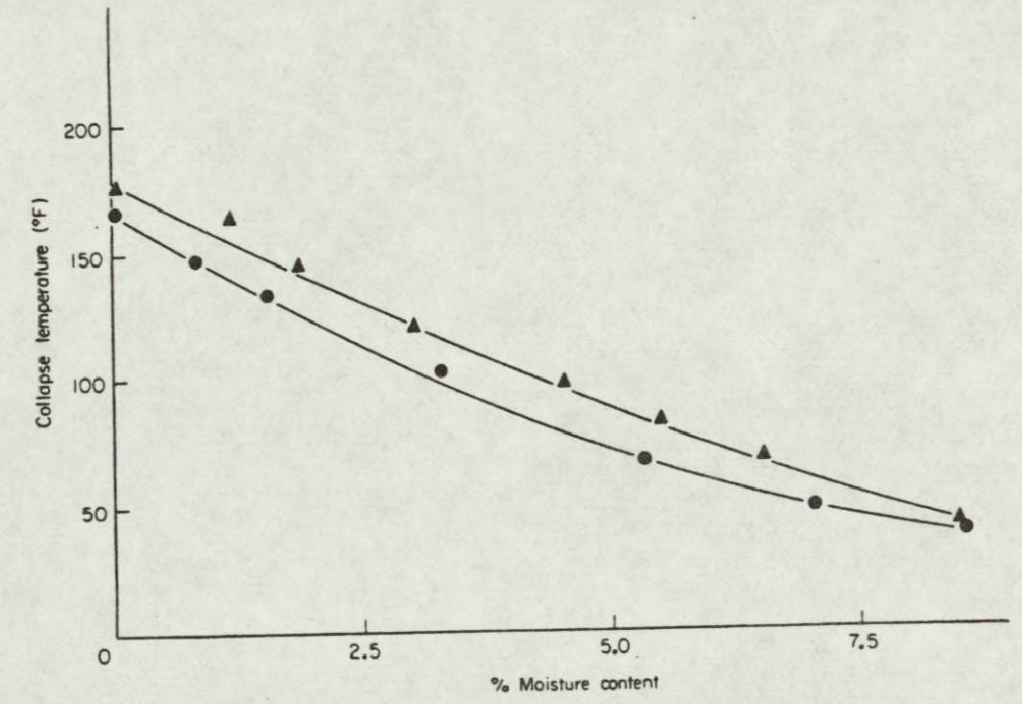

Figure 3. Collapse temperature *vs* moisture content for a mixture of sucrose–maltose (12.5–12.5% solids). ▲, Fast freezing; ●, slow freezing.

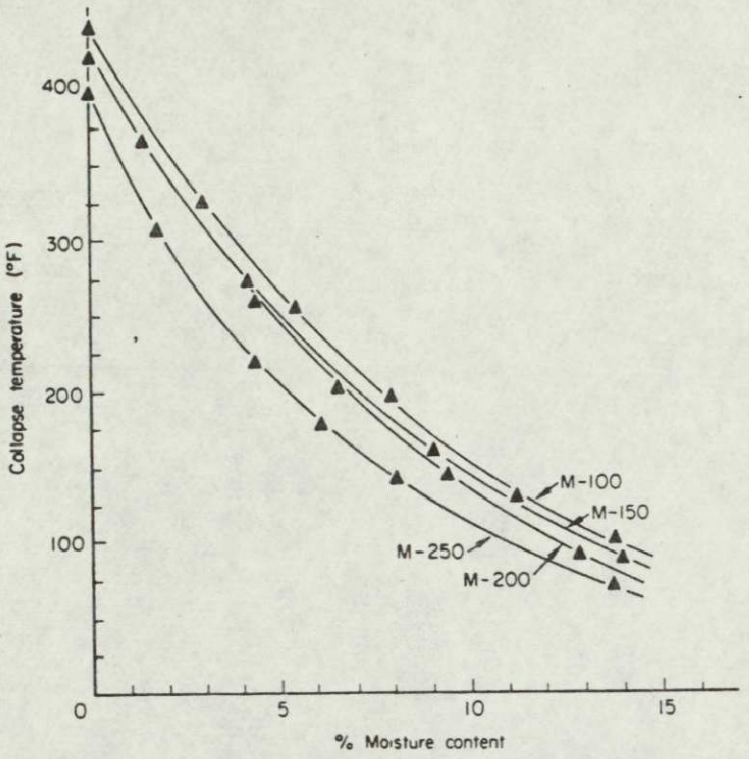

Figure 4. Collapse temperature *vs* moisture content of maltodextrins (25%, w/v).

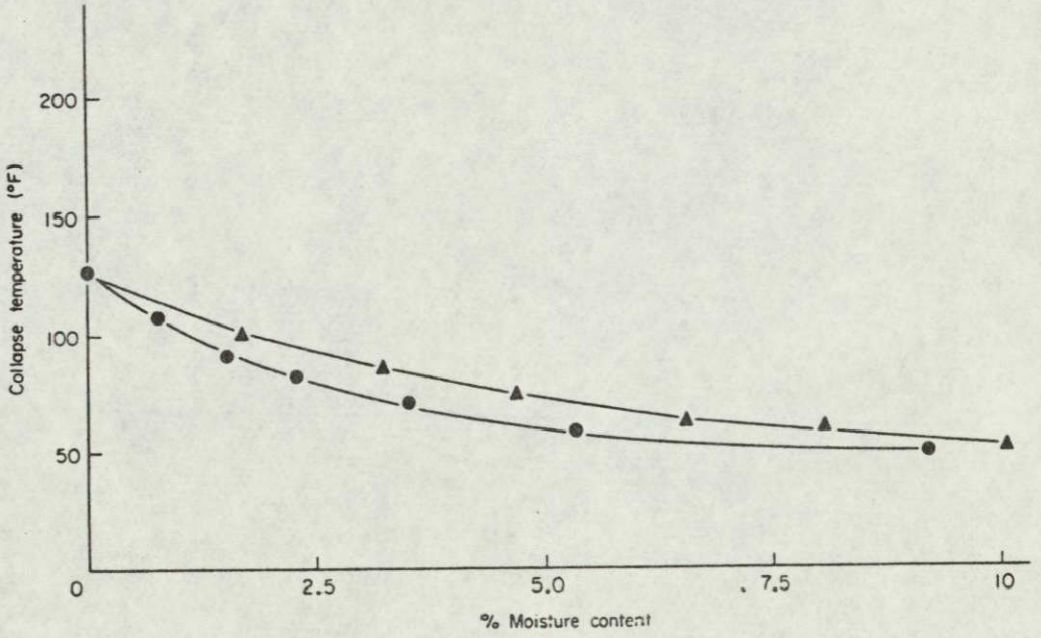

Figure 5. Collapse temperature *vs* moisture content for orange juice (14.2% solids). ▲, Fast freezing; ●, slow freezing.

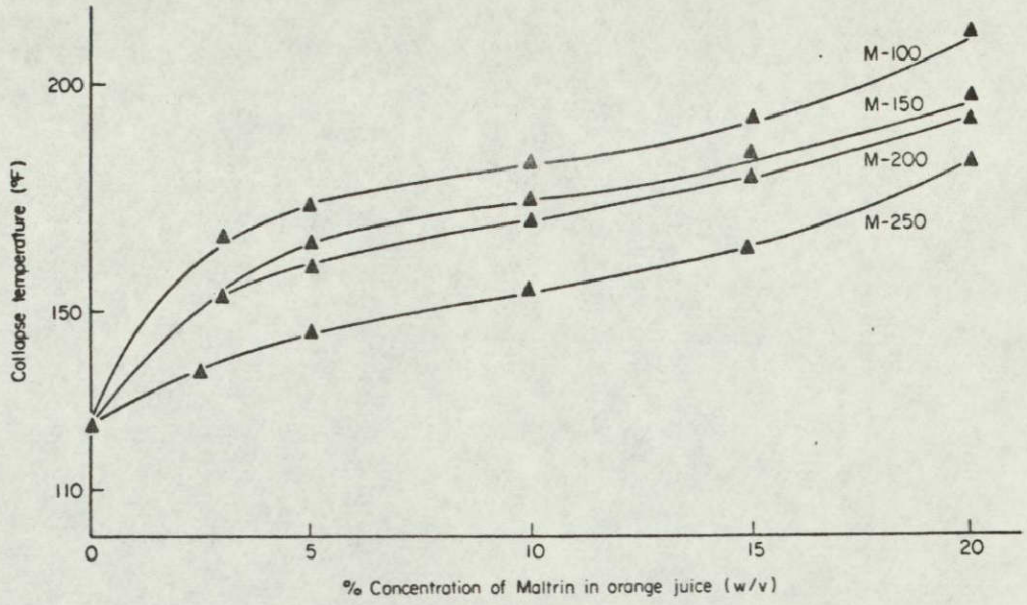

Figure 6. Collapse temperature *vs* concentration of Maltrins in orange juice.

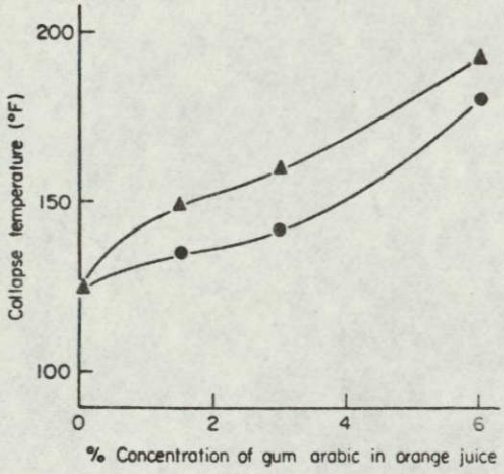

Figure 7. Collapse temperature *vs* concentration of gum arabic in orange juice. ▲, Fast freezing; ●, slow freezing.

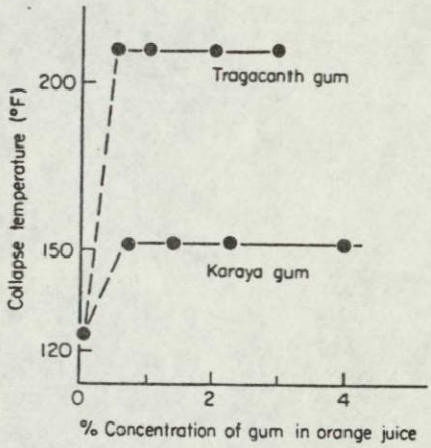

Figure 8. Collapse temperature *vs* concentration of tragacanth gum or karaya gum in orange juice.

Karaya gum has the same effect on collapse temperature at all concentrations tested (up to 4%). As Figure 8 shows, a small amount of karaya gum (around 0.5%) elevates the collapse temperature of orange juice from 125°F (52°C) to 152°F (67°C), and the T_c then remains constant for the whole range of concentrations from 0.5% to 4%. The mode of freezing does not affect the collapse temperature. Tragacanth gum behaves much the same as karaya gum, but the elevation of collapse temperature is much higher (Figure 8).

4. Discussion

The results presented here have described conditions under which dehydrated food materials will undergo loss of structure. The loss of structure is presumably related to the reduction of product viscosity such that under the influences of a variety of forces (gravity, surface tension etc.) the matrix

materials are able to undergo viscous flow. For a particular sample, it appears that a critical level of viscosity exists, and that this viscosity can be achieved by various combinations of moisture content and temperature. Furthermore, within limits, the evaluation of the critical limit of viscosity will depend on the time permitted for observation. Thus, if a shorter time is permitted, it was noted in Figure 1 that a higher sample temperature (i.e. lower viscosity) was required to obtain "collapse".

It was noted that the higher the concentration of the initial solution, the higher the collapse temperature. The initial solute concentration determines the amount of water which remains unfrozen at any given temperature, with concentrated solutions forming less ice than more dilute solutions. The space occupied by ice in the frozen material will ultimately become part of the system of pores and other voids in the dried matrix, provided that no collapse during freeze-drying occurs. Presumably, a system with a smaller fraction of total volume occupied by voids is more resistant to collapse. Less voidage means a smaller number of capillaries, and, therefore, less internal surface area. If surface tension is the driving force for collapse, this would lead to higher collapse temperatures. However, there is an upper limit to the use of preconcentration as a means of achieving higher collapse temperatures, because higher concentrations inhibit ice nucleation.

The rate of freezing for sample preparation appears to have a significant, but relatively small, influence on collapse temperature for solutes of low molecular weight, though the pattern of behaviour for the samples studied is not always the same, even for similar materials such as disaccharides. Freezing rate differences can be considered in terms of nucleation and growth rates of ice crystals. Nucleation rate influences the number of ice crystals formed, and, therefore, the relative sizes of ice crystals (subsequently the pores) and the matrix thickness. Fast freezing increases the number of nuclei formed and means that the distance between ice crystals decreases and therefore the thickness of the matrix decreases. There is the distinct possibility that similar molecular species such as disaccharides will form different bonding arrays on the molecular level. Indeed, in studies in our laboratories, we see that the crystal form for sucrose is quite different from that for lactose or maltose.[11] In this case, the effect of thinner matrix lamella on overall matrix strength can be quite variable from material to material, giving a complex behaviour for the effect of freezing rate on collapse temperature, as observed.

Molecular weight (mol. wt) plays a role in affecting T_c, but is not the sole determinant. In Maltrins, T_c increases with mol. wt, and the T_c's of the Maltrins are also higher than those of disaccharides. However, different disaccharides with the same mol. wt show different T_c values, which, as noted above, may be due to differences in strengths of bonding arrays of the different disaccharides.

Addition of high molecular weight polysaccharides to orange juice resulted in substantial increases in collapse temperature, presumably through increasing the system viscosity. This observation is of practical significance, since for some of the gums tested, significant increases in product structural stability can be obtained with the addition of only small amounts of the gum. This will lead to increased storage life with respect to quality deterioration associated with structural changes (solubility, caking, etc.) and/or to decreased package costs to obtain a given shelf life.

The Amorphous Viscosity Theory of Collapse, which has been developed on the basis of study of the freeze-drying behaviour of solutions, has as its critical variable, the viscosity of the matrix material. Bellows and King[1] reported the critical range of matrix viscosity (called the concentrated amorphous solute) to be between 10^7 and 10^{10} cP (the techniques for measuring the viscosities in this range are quite slow). When the collapse temperatures for freeze-drying materials were included with the data presented here for freeze-dried materials, a smooth curve was obtained. When these pooled data were plotted as ln moisture content *vs* temperature or ln moisture content *vs* reciprocal of the absolute temperature, straight lines were obtained (Figure 9). This indicates that the same critical viscosity range is applicable to both collapse phenomena. Similarly, when the data of Brennan, *et al.*[4] for *sticky-point* temperatures are treated in a similar manner, a similar relationship is obtained.

These observations seem to indicate a simple rapid way for determining the collapse temperatures for concentrated liquid food systems. The collapse temperatures are determined for a number of moisture contents and the results plotted as in Figure 9. Extrapolation of this curve and combina-

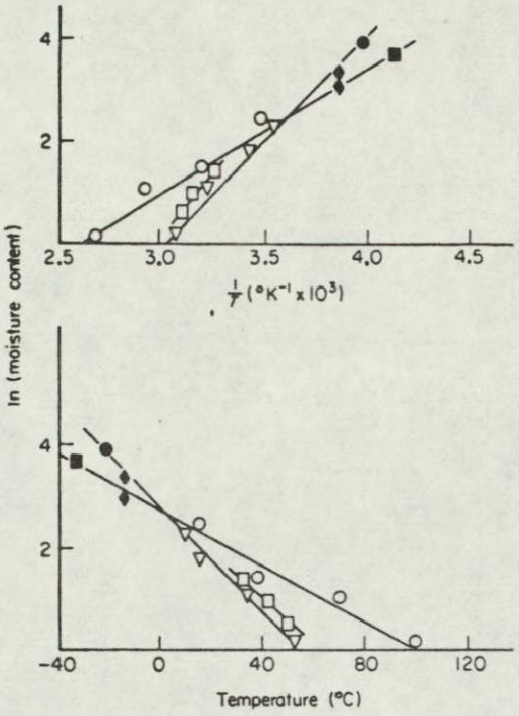

Figure 9. Structural change temperatures *vs* ln moisture content for collapse during freeze-drying,[1] collapse in this work, and sticky-point of orange juice powders.[5] Sucrose: ▽, this work; ●, freeze-drying (ref. 1). Maltose: ○, this work; ◆, flavour loss (ref. 13); ■, freeze-drying (ref. 1). Orange juice–corn syrup solids: □, sticky-point (ref. 4).

tion with the freezing point–concentration curve will give a measure of the collapse temperature for the frozen material.

It was also noted that in earlier studies on loss of model flavour compounds from freeze-dried materials, a critical temperature for release of the volatile from the dry matrix was found. Chirife and Karel[12] noted that encapsulated 1-propanol was not released from freeze-dried maltose at temperatures up to 82°C, but that partial release was obtained at 100°C. In this study, it has been found that the collapse temperature for dry maltose is 96°C (205°F). Thus, release can be related to the loss of structure. A similar observation was reported by Flink and Karel[13] for humidification of volatile containing maltose at low temperature. Their temperature–moisture combination giving loss of volatile lies on the collapse curve of maltose as shown in Figure 9.

While the theory of collapse phenomena has been discussed in the literature primarily in connection with freeze-drying of foods, the results on collapse temperatures obtained in this work are equally applicable to other aspects of food processing.

In agglomeration of dried powders, it is necessary to attain a slight, controlled degree of collapse of the particle surfaces, so that the surface of powder becomes sticky, yet the powder particles remain as discrete units. Examples are given by Jensen.[14] In a method for the industrial production of whey powder (75% lactose) the spray-dryer operates at a low temperature in order to avoid caking of the whey powder while a controlled agglomeration is achieved after the initial drying by increasing moisture content of the powder and then redrying it. Other methods of agglomeration use water vapour to produce a controlled surface collapse which causes the particles to form clusters. These procedures are based on the knowledge that moisture content and temperature determine the potential for collapse. The exact relationship of moisture and temperature for collapse of food materials is required for the design of agglomeration processes which will yield products of high quality. The present study shows these relationships for a number of food materials.

While for agglomeration it is desired to achieve a slight, controlled degree of collapse, in other situations, prevention of collapse is the goal. The sticking of powder in the drying and collecting zones of a spray-drier is related to the collapse phenomenon. Lazar *et al.*,[5] working with tomato juice, passed cooled, atmospheric air of low humidity over the walls of the drier to reduce product

sticking and scorching. Their approach utilised the fact that conditions of low moisture and temperature will prevent collapse. Again, the research conducted in this study provides quantitative information on how the factors of temperature and moisture interact for a number of materials. In addition, the data on the effect of incorporation of additives on "stickiness" allow design of formulated systems which can be more successfully dried.

Another area in which prevention of collapse is essential is the maintenance of quality of dried products during storage, such as prevention of caking of dry powders during storage and loss of flavour compounds from dried materials. Both are associated with collapse behaviour.[7,13]

In this study it has been shown that addition of macromolecules increases the collapse temperature of freeze-dried orange juice. Some of the macromolecules studied gave large increases in collapse temperature at low levels of addition. The observed increase of collapse temperature means that the product will tolerate higher temperatures at a given moisture content without loss of structural qualities. Further, a product packaged in materials of a given water permeability will require more time to reach the critical moisture level for collapse and will therefore have a longer storage life. The above principles apply to other juices and beverages with low collapse temperature, though the collapse temperature of any juice-additive mixture will vary. For example, Moy[15] has shown that added corn syrup or maltodextrins raised the T_c of various tropical fruit juices. Stern and Storrs[16] have shown that the addition of lactose or low-dextrose corn syrup raised the collapse temperature of juices.

Acknowledgements

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4. Artificial Food Matrices (AFM)

4.1 Introduction

Studies on the structural properties and organoleptic suitability of alginate-based artificial food matrices were continued in Phase V. Results of some aspects of these studies have been presented in the scientific literature in papers entitled "Fabrication, Characterization, and Modification of the Texture of Calcium Alginate Gels" (published in J. Food Sci. 42(4):976-981 (1977)) and "A Fruit Simulating Alginate Gel System as a Structured Solid for Studying Food Texture" (anticipated publication date, summer 1978 - presented at the First International Congress on Engineering and Food in August, 1976). Copies of these papers comprise Sections 4.2 and 4.3 respectively. Studies on the cross-linking behavior of the alginate gels, measured by the extent of calcium ion exchange with various replacement ions are noted in Sections 4.4, and Section 4.5 describes studies on the influence of system composition on analysis accuracy for vitamin C in the AFM as well as ascorbic acid stability during AFM manufacture. Studies on production and organoleptic quality of two freeze-dried products incorporating AFM are given in Sections 4.6 and 4.7.

4.2 "Fabrication, Characterization, and Modification of the Texture of Calcium Alginate Gels" by Nancy Luh, James M. Flink, and Marcus Karel (J. Food Sci. 42(4):976-981(1977))

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FABRICATION, CHARACTERIZATION, AND MODIFICATION OF THE TEXTURE OF CALCIUM ALGINATE GELS

ABSTRACT

A simulated fruit gel suitable for freeze dehydration has been developed. The fabricated gel system consists primarily of alginate molecules crosslinked by calcium ions. Static compression tests or compression tests using the Instron Universal Testing Machine were used to characterize the mechanical properties of crosslinked gels having different compositions. It has been observed that incorporation of additional components such as pectin, gelatin, or sucrose to the calcium alginate system modified the textural characteristics of the crosslinked gels. Some hypotheses explaining the effect of added components on gel structure and texture are presented. Comparison of the results obtained from sensory and instrumental methods of texture measurement showed that if the instrumentally measured mechanical properties of two gel samples are different by 20% or more, sensory panelists could differentiate between the two samples at a high level of statistical significance.

INTRODUCTION

SZCZESNIAK (1968) showed that nonuniform cellular structures which simulate fruits and vegetables may be prepared by dialyzing certain alkaline earth metal salts, such as the acid salts of calcium or magnesium, at a uniform rate into an aqueous solution of water soluble alginate at suitable viscosity and concentration. A simulated fruit gel suitable for freeze dehydration has been fabricated by a modified procedure based on the calcium alginate reaction (Luh et al., 1976). In this procedure alginate crosslinking was undertaken within a weak gelatin gel, which was used to allow preliminary solidification and shape formation prior to crosslinking.

Most work in the field of fabrication of simulated fruits has been based on the reaction of calcium ions with soluble alginate or pectate to form a calcium alginate or calcium pectate gel. In some cases fruit puree or fruit pulp has been incorporated as a component of the simulated fruit preparation. For example, black currant pulp was used in the preparation of artificial black currant (Sneath, 1974); apple pulp was used in the preparation of imitation apple slices (Wood and Young, 1972; Unilever, 1974); fruit puree in the preparation of fruit-like alginate gels (Wood and Young, 1974); fruit puree or fruit sauce in "sweetened foods" (Unilever, 1973); and fruit materials in encapsulated fruit products (Young et al., 1973; Unilever, 1971; Wood et al., 1974). Mixed polysaccharide-protein gels, including protein-alginate gels, were also studied by Russian workers who developed asymmetric gel structure useful in formation of food-simulating textures. (Toltogusow et al., 1974; Tolstogusow, 1974, 1975).

In a previous paper a method for producing a food matrix system which simulates fruit texture with good sensory quality and processing stability was reported (Luh et al., 1976). The modification and characterization of texture of this fabricated calcium alginate gel system are reported here. Correlation of sensory and instrumental methods of texture measurement for some of these calcium alginate gels is also presented.

The rheological properties of newly developed food-simulating structures are useful in defining the influence of system composition on texture. In order to be useful as a guide to human response to the developed texture, these properties must be related to organoleptic properties. However, it is well known (Bourne, 1975) that no single rheological measurement adequately describes the totality of the organoleptic concept of texture. In this paper the rheological properties of compressive breaking strength, which is related to cohesiveness, and fracture energy density, which is related to toughness are reported and related to texture.

EXPERIMENTAL

Gel preparation

The method for gel formation and preparation of simulated fruit pieces has been reported previously (Luh et al., 1976). Basically, this consists of first preparing a sodium alginate containing gelatin gel and then crosslinking the alginate in the gelatin gel with calcium ions to form a thermally stable gel of fruitlike properties. The crosslinked gel is then partially dehydrated by osmosis against sucrose and then frozen or freeze dried.

Mechanical properties of the fabricated calcium alginate gels measured by compression tests

Rheological properties of the fabricated calcium alginate gels were evaluated using both static loading compression tests and compression tests using the Instron Universal Testing Machine to measure stress-strain relationships of the fabricated food matrix. In static loading deformation experiments the deformation of gels after sequential addition of static force (weights) was measured by means of a cathetometer. An Instron Universal Testing Machine (Model 1122) was used to perform uniaxial compression of cylindrical gel specimens at a crosshead speed of 20 cm/min. (Shama and Sherman, 1973, have shown that rheological properties obtained by mechanical tests are dependent on the rate of loading, and thus rates as close to those of the mouth during mastication are preferable. The rate of loading used here was the closest to mouth conditions which was available.)

A constant sample surface area has been used (D = 4.2 cm) to eliminate possible complications caused by different surface area. The sample height was approximately 1.5 cm, though *small* variations would be observed between samples. It was impossible to get flat surfaces on large crosslinked gel samples as the center usually bulged outwards, probably because of changes in internal tension and resultant uneven crosslinking density during the crosslinking step. Samples cut from the large gel showed widely varying mechanical properties which depended on their location in the large gel. The reproducibility of measurements of mechanical properties was greatly improved by using smaller molds (5.5 cm diam) to hold the thermally-set gels for the crosslink reaction. The gels were thermally set in the mold and crosslinked by calcium ion diffusion with the mold open face down. A heavy load placed on top of the molds insured flat surfaces of the crosslinked gels.

Correlation of instrumental and sensory methods of texture measurements

Relating instrumental with sensory methods of texture measurement is of interest since objective tests which could substitute for the tedious and time-consuming sensory evaluation would have the advantages of greater speed, ease of standardization, and freedom from drift and other complicating factors associated with panel testing. Also there

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is a desire to explain variations of instrumental values in terms of equivalent human sensations (Kapsalis, 1973).

There are three fundamental types of sensory tests which serve very different functions. Preference/acceptance panels evaluate the opinions, or likes and dislikes, of the consuming public. Discriminatory tests determine whether there are detectable differences among samples. Descriptive tests indicate the kinds or magnitudes of differences among samples (Abbott, 1973).

Triangle tests (discriminatory type) were used to evaluate if panels could detect differences between pairs of samples. The gels varied by the inclusion or omission of one component. Also included in the organoleptic test procedure were evaluations of degree of difference of the samples and choice of descriptive words which best characterize the differences.

RESULTS & DISCUSSION

Static compression tests

Effect of crosslinking. In Figure 1 the effect of crosslinking on the "texture" of the gel can be seen by comparing the two force-deformation curves for gelatin gel systems containing 2.0% alginate, 2.0% pectin and 30% sucrose. As expected, crosslinked gels are much firmer than noncrosslinked gels, a very small force causing a large deformation of the noncrosslinked thermal gel. Alginate concentration also has an effect on the mechanical properties of the crosslinked gels in that increasing alginate concentration gives crosslinked gels of increased firmness.

Major sources contributing to texture of the crosslinked gels. The deformation behavior of 2.5% alginate gels containing various combinations of pectin, gelatin, and sucrose was similar to the pure 2.5% alginate gel (shaded area in Fig. 1), indicating that calcium alginate is the primary contributor to the firm texture of the crosslinked gels and that the other components only act to modify this basic texture.

Compression test using the Instron Universal Testing Machine

In compression testing, the Instron Universal Testing Machine applied force perpendicularly to the surface of the sample. It was noted that the sample also expands radially while it is compressed perpendicularly by the downward moving crosshead. It is thus possible that final fracture of a sample undergoing a compression test may be caused by tension forces perpendicular to the direction of the applied compression force. Nevertheless, it is felt that the rheological data obtained in compression are related to cohesiveness and toughness.

Effect of gelation agents and type of gelation on mechanical properties of gelled systems. To evaluate the effect of type of gelation on mechanical properties, systems containing various combinations of the two gelling components, sodium alginate (2.5%) and gelatin (1.5%), were prepared as thermoset gelatin gels or crosslinked calcium alginate gels. Table 1 gives the mechanical properties for the various combinations obtained.

The effect of crosslinking after the thermal setting of the gelatin gel on the mechanical properties can be seen by comparing the values for systems (B) and (C). The increase in firmness (tangent moduli at various strains), strength (stress at breaking point), and toughness (fracture energy density) which results from the crosslinking of the alginate molecules with calcium ions is readily apparent. This is in agreement with the results from the static loading tests as noted above.

Comparison of systems (C) and (D) shows the effect of gelatin on some of the mechanical properties of the crosslinked gels. The increased strength and toughness of gelatin-containing crosslinked gels cannot be accounted for by the strength and toughness of the gelatin gel alone, which is quite weak, as is shown by system (A).

Possible mechanisms by which gelatin may alter the mechanical properties have been investigated. They are:

(a) Interaction of gelatin with the crosslinking agent calcium lactate. To test if gelatin will form a more rigid gel in the presence of calcium lactate, a 1.5% (w/v) gelatin gel was placed in a calcium lactate solution (4.5% (w/v)) for 60 hours at room temperature to allow any possible interaction to occur. No evidence of crosslinking was observed after this time, and in fact the gelatin gel became weaker because of partial dissolution.

(b) Changed rate and pattern of alginate crosslinking because of gelatin interfering with the diffusion of calcium ions. The rate of crosslink formation in 2.5% (w/v) alginate gels containing 1.5%, 2.0%, 2.5%, or 3.0% (w/v) gelatin was studied. The method is the same as described by Luh et al. (1976). No effect of gelatin concentration on the rate of formation of calcium alginate gel was noted.

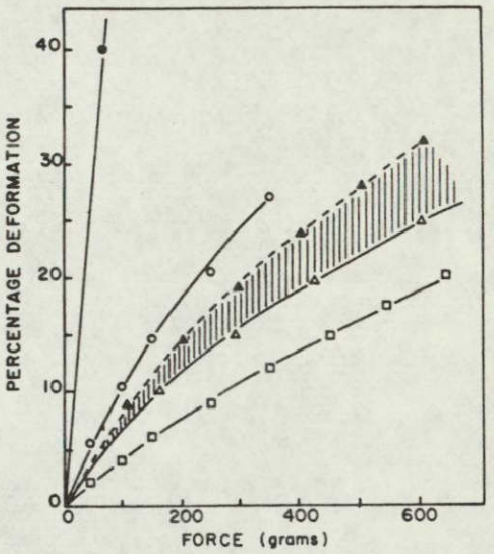

Fig. 1—Load-deformation behavior of fabricated gel systems containing 1.5% gelatin, 2.0% pectin and 30% sucrose: • Noncrosslinked thermal gel (2.0% alginate); ○ Crosslinked gel (2.0% alginate); △ Crosslinked gel (2.5% alginate); □ Crosslinked gel (3.0% alginate). Shaded area indicates range of values for the following gels: 2.5% alginate; 2.5% alginate, 2% pectin; 2.5% alginate, 2% pectin, 30% sucrose; 2.5% alginate, 2% pectin, 30% sucrose, 1.5% gelatin.

Table 1—Mechanical properties of gelatin and alginate based gels

		Sample properties			
		A	B	C	D
Gelatin —		1.5%	1.5%	1.5%	0%
Alginate —		0%	2.5%	2.5%	2.5%
Crosslinked —		No	No	Yes	Yes
Tangent moduli at strain	0.3	0.17	0.40	10	4
(kg/cm^2)	0.5	0.44	0.50	23	12
Breaking strength (kg/cm^2)		0.12	0.19	6.4	5.6
Fracture energy density ($kg\text{-}cm/cm^3$)		0.023	0.04	1.0	0.90

(c) Gelatin acting as a "filler" in the crosslinked calcium alginate network. Hardness and strength of mixtures cannot be interpolated from the values for the pure mixture components since there are interactive effects. For example, a finely dispersed, rigid particle inhibits slip and prevents shear of a ductile matrix (Van Vlack, 1964). Therefore, it is possible that the soft gelatin gel, when incorporated with the alginate, may enhance the strength of the mixed crosslinked calcium alginate to a greater extent than the strength attributed to the gelatin gel itself.

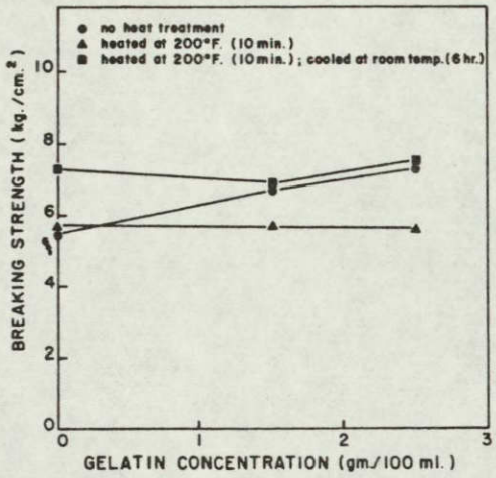

Fig. 2—Effect of heat treatment on the breaking strength of 2.5% alginate gels of different gelatin concentration.

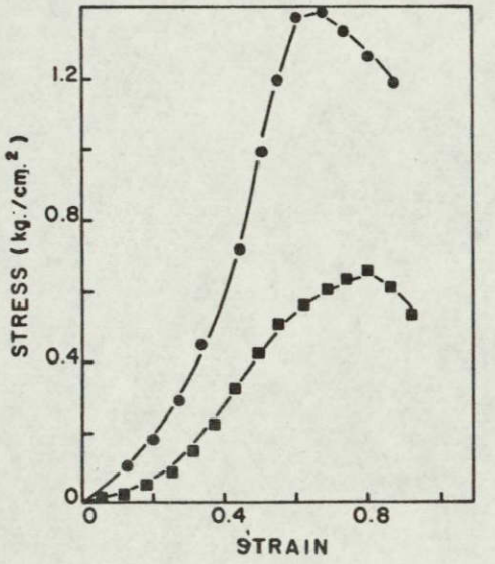

Fig. 3—Effect of sucrose on stress-strain behavior of gels containing 2.5% alginate, 1.5% gelatin and 2.0% pectin (high level of esterification); (●: 0% sucrose; ■: 30% sucrose).

If gelatin influences the mechanical properties of crosslinked alginate gels by existing in the gel state in the calcium alginate structure, it can be expected that the mechanical properties of the gelatin-containing crosslinked gels will be temperature sensitive. Gels heated in water at 90°C for 10 min were subjected to compression tests either immediately after heating while the samples were still hot or after being cooled in water at room temperature for 6 hr.

Figure 2 shows the breaking strengths of the gels as a function of gelatin concentration for the different treatments. Samples containing different concentrations of gelatin which were tested while still hot showed similar breaking strengths. At the elevated temperature the gelatin no longer influences the breaking strength, indicating that the gelatin gel behaves as an independent filler in the crosslinked alginate gels. At room temperature the gelatin gel structure reinforces the alginate structure, while at the elevated temperatures at which the gelatin no longer exists in the gel state, there is little effect of gelatin concentration. When the gelatin gel resets after the cooling step, the reinforcement returns.

It was noted that after heating and cooling, the alginate gel without gelatin had a higher breaking strength than prior to treatment, which may be because of an increased crosslinking density induced by heating. The presence of gelatin may inhibit increased crosslinking effects in the gelatin containing samples. Heating also resulted in an irreversible loss of water from the gel; soaking the heated gel in water for 6 hr did not give an increase in gel moisture content.

Effect of nongelling components on the mechanical properties of the fabricated food matrix. *Sucrose.* The effect of sucrose on the stress-strain behavior of one multicomponent fabricated food matrix system is shown in Figure 3, while the influence of sucrose on selected mechanical properties for gelled systems of varying complexity is given in Table 2.

One possibility is that sucrose behaves as a plasticizer in that the mechanical strengths are weakened by the incorporation of sucrose into the gelling system. Examination of the stress-strain curves also shows a change of breakdown pattern of the sucrose-containing gels with less sharp and abrupt breaking points which indicates some flow occurred before final failure (Fig. 3). Other possibilities which cannot be entirely excluded are changes in the state of water in the gel because of the presence of sucrose and potential interference of sucrose with Ca^{++} ion diffusion.

Pectin of two levels of esterification. The influence of pectin at two levels of esterification on the stress-strain behavior

Table 2—Effect of sucrose on the mechanical properties of some gels

Gel composition[a]	N[b]	Breaking strength (kg/cm²)	Fracture energy density (kg-cm/cm³)
A	11	5.45 ± 0.15	0.923 ± 0.016
A, S	11	3.64 ± 0.18	0.814 ± 0.026
A, G	11	6.01 ± 0.18	1.045 ± 0.036
A, G, S	9	2.85 ± 0.27	0.571 ± 0.011
A, G, P-L	9	1.99 ± 0.21	0.413 ± 0.028
A, G, P-L, S	9	1.03 ± 0.06	0.262 ± 0.015
A, G, P-H	8	1.34 ± 0.05	0.395 ± 0.008
A, G, P-H, S	10	0.65 ± 0.04	0.246 ± 0.013

[a] A = Alginate (2.5%); S = Sucrose (30%); G = Gelatin (1.5%); P = Pectin (2%), (L, H: Low or High Level of Esterification).
[b] Number of samples

of the gels are shown in Figure 4. It is seen that pectins of both levels of esterification weaken the mechanical strength of the gels, though in all cases the pectin of higher level of esterification gives the weaker of the pectin-containing gels (Table 3). The fact that pectin of low level of esterification (around 30%) can itself form a weak solid gel with calcium ions (Table 3) while pectin of high level of esterification (around 70%) does not could account qualitatively for the differences, though other factors (for example, possible differences in pectin molecular structure) could be responsible.

Increasing the pectin concentration does not result in a further major decrease of mechanical strength of the fabricated gels. Incorporation of pectin and sucrose gives a synergistic weakening of the mechanical strength of the fabricated gel.

Other potential texture modifers. Table 4 shows the effect of the addition of some nongelling (under the conditions used here) materials such as polyvinyl alcohol (PVA), carboxymethylcellulose (CMC), microcrystalline cellulose (Avicel), and lysine on the mechanical properties of a 2.5% alginate system. (In this case one step gelation was used as no gelatin was included.) It can be seen that all the added nongelling materials give a weakening of the mechanical properties of the resultant gelled matrix.

Some thoughts on the structure of the fabricated food matrix system

It is believed calcium alginate gels result from the formation of junction zones composed of stacks of alginate molecules with calcium ions packed between the alginate chains (Rees, 1969, 1972). When other materials are incorporated, a calcium alginate gel is still able to form, but the mechanical properties of such gels are different from those of the pure calcium alginate gels. The physical chemistry of multicomponent gel systems is very complex, and little information is available at present.

It can be reasonably speculated that calcium alginate gels formed in the presence of other materials are still crosslinked frameworks of junction zones of stacked alginate molecules which are basically the same as those present in pure calcium alginate gels. The changed mechanical properties of multicomponent gels may result from:

1. Changes of junction zone size in which the number of residues of *each* alginate molecule participating in junction zone formation is affected by the presence of other materials. The number of alginate chains involved in a given junction zone would also be affected by the presence of other materials.

2. Changed distribution of junction zones in the gel, where the distribution (number and density) of junction zones is expected to change when other materials are incorporated in the alginate system.

3. Interaction between the noncrosslinked portion of the alginate chains and the incorporated materials.

The changed-size junction zone, which could be because of

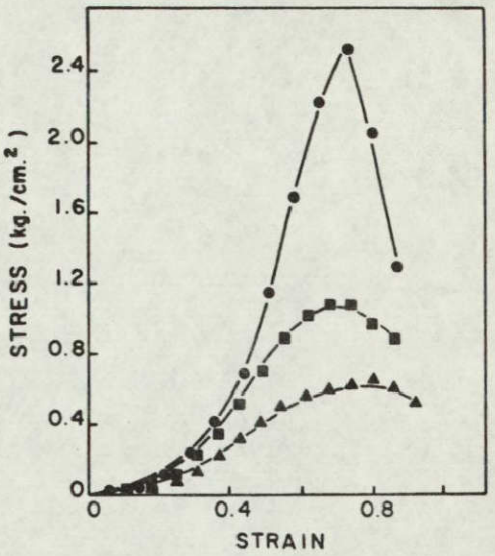

Fig. 4—Effect of level of esterification of pectin on stress-strain behavior of gels containing 2.5% alginate, 1.5% gelatin and 30% sucrose; (●: 0% pectin, ■: 2.0% pectin of low esterification, ▲: 2.0% pectin of high esterification).

Table 3—Effect of pectin and its level of esterification on the mechanical properties of the gels

Gel composition[a]	N[b]	Breaking strength (kg/cm²)	Fracture energy density (kg-cm/cm³)
A	11	5.45 ± 0.15	0.923 ± 0.016
A, P-L 1.0%	10	3.40 ± 0.16	0.546 ± 0.036
A, P-L 2.0%	10	3.30 ± 0.10	0.535 ± 0.020
A, P-H 2.0%	8	1.54 ± 0.17	0.256 ± 0.011
A, P-H 3.0%	9	1.09 ± 0.10	0.203 ± 0.015
A, G	11	6.01 ± 0.18	1.405 ± 0.036
A, G, P-L 2.0%	9	1.99 ± 0.21	0.413 ± 0.028
A, G, P-H 2.0%	8	1.34 ± 0.05	0.395 ± 0.008
A, G, S	9	2.85 ± 0.27	0.571 ± 0.011
A, G, P-L 2.0%, S	9	1.03 ± 0.06	0.262 ± 0.015
A, G, P-H 2.0%, S	10	0.65 ± 0.04	0.246 ± 0.013
2.0% P-L	5	0.88 ± 0.07	0.195 ± 0.011

[a] A = Alginate (2.5%); S = Sucrose (30%); G = Gelatin (1.5%); P = Pectin, (L, H = Low or High level of Esterification).
[b] Number of samples

Table 4—Effect of some polymeric and nonpolymeric materials on the mechanical properties of calcium alginate gels

Gel composition[a]	N[b]	Breaking strength (kg/cm²)	Fracture energy density (kg-cm/cm³)
A	11	5.45 ± 0.15	0.923 ± 0.016
A, PVA 0.5%	10	2.05 ± 0.23	0.435 ± 0.011
A, PVA 1.0%	10	2.46 ± 0.28	0.469 ± 0.020
A, PVA 2.0%	12	2.67 ± 0.15	0.488 ± 0.023
A, CMC 0.5%	10	1.75 ± 0.06	0.334 ± 0.006
A, CMC 1.0%	10	1.83 ± 0.10	0.317 ± 0.008
A, CMC 2.0%	10	0.97 ± 0.04	0.174 ± 0.004
A, avicel 1%	11	3.79 ± 0.24	0.584 ± 0.012
A, avicel 2%	11	3.88 ± 0.30	0.650 ± 0.021
A, lysine 0.5%	10	3.14 ± 0.22	0.598 ± 0.039
A, lysine 1.0%	10	3.74 ± 0.19	0.666 ± 0.036

[a] A = Alginate; PVA = Polyvinyl alcohol; CMC = Carboxymethylcellulose.
[b] Number of samples

either fewer monomeric units of each alginate molecule participating in junction zone formation or a different number of alginate chains being involved in a given junction zone, could result from the incorporated material either sterically hindering alginate chain mobility, modifying the properties of water molecules or calcium ions, or associating with alginate chains, etc. It is known that the cooperative association of alginate and calcium ions gives a structure of high stability. Before two chains in a junction zone can come apart, all of the individual links in the junction zone must be severed simultaneously. If the probability of a single link coming apart and staying apart over a given time interval is one in two, the probability of dissociation of a junction zone 20 units long is 1 in 2^{20}, about one chance in a million. If the incorporation of nongelling material reduces the size of each junction zone, the mechanical strength of the crosslinked calcium alginate would be expected to be weaker by an exponential factor related to the reduction in junction zone size.

Table 5—Texture evaluation of gels with different compositions[a]

Triangle test	A	AGS	AS	AGPS
	A	AS	AGPS	AGPS
	AG	AGS	AS	AGS
Check odd sample[b]	6/15	11/15	15/15	15/15
Level of statistical significance	N.S.	1%	0.1%	0.1%
Degree of difference[c]				
Slight	5	6	0	1
Moderate	1	3	1	2
Much	0	2	9	9
Extreme	0	0	5	3
Preference		AGS:AS 10:1	AGPS:AS 12:2	AGPS:AGS 12:1
Characterization of differences				
Toughness		6 AS		12 AGS
Softness		1 AS	10 AGPS	
Chewiness		1 AS		4 AGS
Tenderness			6 AGPS	
Juiciness		1 AS	3 AS	
Dryness		2 AS		2 AGS
Crispness		2 AS		4 AGS
Sogginess			3 AGPS	

[a] Gel compositions A = Alginate (2.5%); G = Gelatin (1.5%); S = Sucrose (30%); P = Pectin (2%), (High Level of Esterification).
[b] n_2/n_1 : n_1 is the total number of panelists; n_2 is the number of panelists that can distinguish the odd sample from duplicates.
[c] Number refers only to those who can correctly distinguish the odd sample from the duplicates.

Two views of the influence of added materials on junction zone distribution are:

1. A larger number of widely distributed junction zones, each of a smaller size (compared to that of a pure calcium alginate gel), are formed in the presence of other materials.
2. Junction zones are concentrated at selected locations in the network in the presence of other materials.

A uniform and homogeneous distribution of the alginate molecules in the solvent is expected since a homogenization step is involved in the preparation of alginate mixture before crosslinking. This procedure would favor more, smaller junction zones that are widely distributed throughout the framework of the calcium alginate gel. However, in the two-step procedure used for the gel preparation, a soft gelatin gel was set prior to the crosslinking step. This could result in molecular arrangements occurring during the setting of the gelatin gel which would give a nonuniform distribution of alginate molecules. It is known that the network links are widely spaced in a gelatin gel, and the regions between the links are highly flexible. It is probable that the alginate molecules are nonuniformly distributed in the regions between the links of the gelatin gel.

Studies on the mechanical behavior of materials of varying bonding uniformity would indicate that a calcium alginate gel with uniformly distributed junction zones will have a higher mechanical strength than the calcium alginate gel with an equal number of junction zones nonuniformly distributed since local molecular flow tends to occur more readily with nonuniformly distributed crosslinked network. However, it is not known whether the possible rearrangement of alginate molecules by the gelation of gelatin gel will affect the size as well as the total number of junction zones.

In addition to interference at the junction zones, there can also be interactions between the noncrosslinked portion of alginate chains and the incorporated materials. The precise nature of these interactions are not known.

Correlation of instrumental and sensory "texture" measurements

"Texture" of various gel samples was evaluated by sensory and instrumental methods. Table 5 summarizes the results obtained in the sensory tests, while Table 6 gives the mechanical properties of each sample as measured by compression tests using the Instron Universal Testing Machine. Table 7 shows the degree of difference of the measured mechanical properties for each pair of samples. From Table 5 it can be seen that the panelists can distinguish differences in texture of pairs AS/AGS, AS/AGPS, and AGS/AGPS at a high level of statistical significance (A = alginate, G = gelatin, S = sucrose, P = pectin). This correlates to differences of mechanical properties of at least 20% (Table 7). It was noted that when gelatin was the varied component, most panelists listed the differences between samples as "slight," while when pectin (with a high level

Table 6—Mechanical properties of gels with different compositions

Gel composition[a]	N[b]	Breaking strength (kg/cm^2)	Fracture energy density ($kg\text{-}cm/cm^3$)
A	11	5.45 ± 0.15	0.923 ± 0.016
AG	11	6.01 ± 0.18	1.046 ± 0.036
AS	11	3.64 ± 0.21	0.814 ± 0.022
AGS	9	2.85 ± 0.26	0.571 ± 0.037
AGPS	10	0.65 ± 0.04	0.246 ± 0.013

[a] See note "a," Table 5.
[b] N refers to the number of samples tested.

Table 7—Degree of difference[a] *of the measured mechanical properties within each pair of samples*

Sample pairs[b]	Breaking strength (kg/cm^2)	Fracture energy density ($kg\text{-}cm/cm^3$)
A/AG	9.32%	11.68%
AS/AGS	21.70%	29.85%
AS/AGPS	82.14%	69.78%
AGS/AGPS	77.20%	56.92%

[a] For example, in pair A/AG the degree of difference of breaking strength is calculated as [(6.01 − 5.45)/6.01] × 100.
[b] See note "a," Table 5.

of methyl esterification) was the varied component, the differences were called "much." Also, the word used most frequently to describe the difference in texture for matrices without pectin was "toughness," while "softness" was used for matrices containing pectin. Since fracture energy density is the mechanical property considered to indicate the toughness of a food, it would seem to be the most appropriate property to measure to describe texture differences of the fabricated food matrices.

Although a definite difference was measured by the Instron machine for the pair A/AG, the panelists failed to find a difference between the two samples. This is attributed to the smaller percentage difference between the measured mechanical properties of the samples. It should be noted that the pair A/AG is the only pair without sucrose, and it is possible that the influence of sweet taste on the evaluation of textural characteristics might affect the accuracy of the texture evaluation.

It is concluded that at the levels of incorporation of pectin associated with the improvement of the sensory qualities of the fabricated food matrix, differences in sample "texture" can be measured by instrumental methods and well perceived by panelists. In general, it seems that the Instron Universal Testing Machine can detect smaller differences of mechanical properties among samples than panelists can detect by sensory testing.

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4.3 "A Fruit Simulating Alginate Gel System as a Structured Solid for Studying Food Texture" by Nancy Luh, James Hawkes, James M. Flink, and Marcus Karel.

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A Fruit Simulating Alginate Gel System as a Structured Solid for Studying Food Texture

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ABSTRACT

The changes of mechanical properties associated with the addition of various components to an alginate-based gelling system have been evaluated. It has been shown that the presence of gelatin, which is itself gelled prior to the alginate crosslinking, results in increased values of breaking strength and fracture energy density; all other compounds incorporated resulted in reduced values. An analysis of the distribution of calcium in the gel indicates that the amount of calcium involved in gel structure formation (i.e. junction zones) was not influenced by the addition of sucrose and/or pectin to the initial mixture. Analysis of replicate samples demonstrated that the alginate gel system is highly suitable as a reproducible test material for food texture studies.

INTRODUCTION

Foods are complex systems exhibiting various degrees of elasticity, viscosity, and plasticity. Because of the complex structure and mechanical behavior of foods, objective measurements of food texture may be influenced by a variety of test conditions, including rate of loading, the magnitude of deformation imposed upon the material, geometry of the loading surface, and localized yielding within the product (Finney, 1969). Bourne (1975) emphasized that texture is not a single-point measurement, and proposed "textural porperties" as a more appropriate terminology. Due to the complexity of food systems and still limited understanding of the mechanical behavior of food materials, a meaningful objective measurement which relates the mechanical properties with the sensory properties of the food material is not easily achieved. One unavoidable problem encountered in food texture studies is the lack of reproducibility of food samples. Many factors such as variety, season, maturity, age, etc affect the reproducibility of the food samples, and thus, reproducible texture studies are very difficult to achieve using conventional food systems. If it is desired to evaluate the affect of processing or testing conditions on the texture of a

food, it is essential that reproducible initial samples be available. A model food system fabricated from known materials offers the advantage that its properties are independent of factors such as availability, maturity, etc; their behavior should be reproducible and predictable as long as the starting materials do not change and that defined procedures for fabrication are followed.

Study of the relationship between composition and texture using a real food system is difficult since the structure and composition tend to be quite complex. A fabricated food system offers some advantage over the conventional food system since the composition can be changed systematically. This makes it possible to study the interaction of different components and the relationship between composition and texture of food systems. Knowledge obtained from these type of studies are necessary for development of food fabrication processes.

This paper reports mechanical properties of a fruit simulating alginate gel system which can be used as a structured solid for studying food texture. The mechanical properties of this system have been shown to be highly reproducible. The effect of composition change on mechanical properties is presented.

EXPERIMENTAL METHODS

Gel Preparation

The method for gel formation and preparation of simulated fruit pieces has been reported previously (Luh et al, 1976). A sodium alginate containing gelatin gel is prepared and then the alginate in the gelatin gel is crosslinked with calcium ions to form a thermally stable gel of fruitlike properties.

A mass balance on the gel and crosslinking solution was conducted to determine the transport of solids and water during crosslinking of a variety of alginate gelling systems. The changes of total solids and water content were determined from differences of the original and final wet weight and dry weight (after freeze drying) of gel samples and aliquots of the crosslinking solution. The calcium content of the gels and solutions were analyzed according to the AOAC methods using EDTA (36.054, 12th edition). The calcium content of the alginate gel was classified into two fractions, "bound" and "free". The gel samples were freeze dried, pulverized and then soaked for 24 hours in distilled water. The fraction which was leached from the pulverized powder is termed "free", while that retained in the gel following the 24 hour soak is considered to be "bound". Loss of gelatin from the gelling system was evaluated by determining Kjeldahl nitrogen in the crosslinking solution by the AOAC microKjeldahl procedure (47.021).

Evaluation of Mechanical Properties by Compression Tests

Rheological properties of the fabricated calcium alginate gels were evaluated by compression tests using static loading or the Instron Universal Testing Machine. In static loading experiments the cumulative deformation of gels was measured with a cathetometer after sequential addition of static force (weights). An Instron Universal Testing Machine (Model 1122) was used to measure stress-strain relationships during uniaxial compression of cylindrical gel specimens at a cross-head speed of 20 cm/minute. The stress-strain curves were used to obtain the following mechanical properties:

1) Tangent Moduli: slope of the stress-strain curve at the designated strains

2) Breaking Strength: applied stress per unit cross-sectional area at point of sample rupture (maximum of stress)

3) Fracture Energy Density: area under stress-strain curve from zero strain to strain at rupture.

In initial evaluations of mechanical properties, samples having a constant cross-sectional area were obtained by cutting the samples from a larger slab with a 4.2 cm (i.d.) cork borer. The sample height was approximately 1.5 cm, though small variations were noted between samples. With large crosslinked gel samples,

it was impossible to get flat surfaces as the center usually bulged outwards, probably because of changes in internal tension and resultant uneven crosslinking density during the crosslinking step. Thus samples cut from the large gel showed widely varying mechanical properties which depended on their location in the large gel. The reproducibility of mechanical properties measurements was greatly improved by using smaller molds (5.5 cm diameter) to hold the thermally-set gels for the crosslink reaction. The gels were thermally set in the mold and crosslinked by calcium ion diffusion with the mold open face down. A heavy load placed on top of the molds insured flat surfaces of the crosslinked gels.

Some fruits were also evaluated for mechanical properties to allow comparison with the properties measured for the fruit-simulating calcium alginate gel. Fruits obtained at a local supermarket were hand peeled, sliced to the desired thickness, and cylindrical disks cut from the slices using a 4.2 cm (i.d.) cork borer with sharpened edges.

Compression tests were conducted with an Instron Universal Testing Machine (Model TT-B) operated at the following conditions:

Crosshead speed: 5 cm/minute

Chart speed: 50 cm/minute

Cross-sectional area of the samples: 13.8 cm^2

(except banana due to natural limitiation)

Height of the sample: approximately 1.5 cm

RESULTS AND DISCUSSION

COMPRESSION TESTS BY STATIC LOADING

Comparisons of force-deformation curves from static compression tests can demonstrate the basic differences in rheological properties associated with composition changes (Figure 1). The effect of crosslinking on the "texture" of the gel can be seen by comparing the two force-deformation curves for gelatin gel systems containing 2.0% alginate, 2.0% pectin, and 30% sucrose. As expected, crosslinked gels are much firmer than noncrosslinked gels. Increasing the alginate concentration results in sizable increases in firmness following crosslinking. A series of 2.5% alginate gels containing various combinations of pectin, gelatin, and sucrose showed similar deformation behavior (shaded area in Figure 1), indicating that calcium alginate is the primary contributor to the firm texture of the crosslinked gels and that the other components act only to modify this basic texture.

COMPRESSION TESTS USING THE INSTRON UNIVERSAL TESTING MACHINE

In compression testing, it was noted that the sample expands radially while it is being compressed perpendicularly by the downward moving crosshead of the Instron tester. Final fracture of a sample undergoing a compression test may therefore be caused by tension forces perpendicular to the direction of the

applied compression force. Nevertheless, it is felt that the rheological data obtained in compression tests are related to cohesiveness and toughness.

Effect of Gelation Agents and Type of Gelation on Mechanical Properties of Gelled Systems

Various combinations of the two gelling components, sodium alginate (2.5%) and gelatin (1.5%), were prepared as thermoset gelatin gels or crosslinked calcium alginate gels, and mechanical properties determined (Table 1). The effect of crosslinking of the alginate molecules on the mechanical properties of the complex interpenetrating gel is obtained by comparing the values for systems (B) and (C). The increase in firmness (tangent moduli at various strains), strength (stress at breaking point), and toughness (fracture energy density) is in agreement with the results from the static loading tests. The increased strength and toughness associated with the presence of gelatin in crosslinked gels (compare systems C and D) cannot be accounted for by the strength and toughness of the gelatin gel alone, which is quite weak (system A). It appears therefore that gelatin modifies in some way the texture of the crosslinked gel. To obtain further information on possible mechanisms by which gelatin may alter the mechanical properties the following investigations were made.

(a) Tests to show if gelatin will form a more rigid gel in the presence of the crosslinking agent, calcium lactate, gave no

indication of crosslinking after 60 hours; the gelatin gel, in fact, became weaker because of partial dissolution.

(b) The rate of crosslink formation (method given in Luh et al, 1976) in 2.5% (w/v) alginate gels containing 1.5%, 2.0%, 2.5%, or 3.0% (w/v) gelatin was evaluated to see if gelatin could interfere with calcium ion diffusion, giving changes in the rate and/or pattern of alginate crosslinking. Gelatin concentration showed no effect on the rate of formation of calcium alginate gel.

(c) Gelatin acting as a "filler" in the crosslinked calcium alginate network may enhance the strength of the mixed crosslinked calcium alginate to a greater extent than the strength attributed to the gelatin gel itself. It is known that hardness and strength of mixtures cannot be interpolated from the values for the pure mixture components since there generally are interactive effects. (Van Vlack, 1964).

If gelatin influences the mechanical properties of crosslinked alginate gels by existing in the gel state in the calcium alginate structure, the mechanical properties of the gelatin-containing crosslinked gels should be temperature sensitive. Gels heated in water at 90°C for 10 minutes were subjected to compression tests either immediately after heating while the samples were still hot or after being cooled in water at room temperature for six hours.

Increasing the gelatin concentration gave increases in breaking strength for the unheated samples. At the elevated

temperature the gelatin no longer influences the breaking strength, indicating that the gelatin gel behaves as an independent filler in the crosslinked alginate gels. At room temperature the gelatin gel structure reinforces the alginate structure, while at the elevated temperatures at which the gelatin no longer exists in the gel state, there is little effect of gelatin concentration. When the gelatin gel resets after the cooling step, the reinforcement returns.

Effect of Nongelling Components on the Mechanical Properties of the Fabricated Food Matrix

Studies on changes of mechanical parameters due to incorporation of non-gelling components into the Fabricated Food Matrix were conducted using a number of replicate gels. The results of these studies show that the gel-to-gel reproducibility of the mechanical parameters is very good, the standard deviation being less than $\pm$10% of the mean (and generally 5% or below) (Tables 2, 3, 4).

(a) Sucrose

The influence of sucrose on selected mechanical properties for gelled systems of varying complexity is given in Table 2. In all cases the mechanical strength is weakened by the incorporation of sucrose into the gelling system. Besides the reduction in breaking strength, the stress-strain curves also show less sharp breaking points indicating that some flow occurred before final failure. Sucrose may therefore act as

a plasticizer. Other possibilities include: a.) changes in the state of water in the gel because of the presence of sucrose and b.) the interference by sucrose with the rate of Ca^{++} ion diffusion (Luh et al, 1976).

(b) Pectin of two levels of esterification

Pectins at high or low levels of esterification weaken the mechanical strength of the gels, though in all cases the pectin of higher level of esterification gives the weaker of the pectin-containing gels (Table 3). The fact that pectin of low level of esterification (around 30%) can itself form a weak solid gel with calcium ions (Table 3) while pectin of high level of esterification (around 70%) does not, could account qualitatively for the differences, though other factors, such as, differences in pectin molecular structure could be responsible. Incorporation of pectin and sucrose gives a synergistic weakening of the mechanical strength of the fabricated gel. (Tables 2, 3).

(c) Other potential texture modifier

Polymeric materials which will not form gels under the conditions used here (polyvinyl alcohol (PVA), carboxymethylcellulose (CMC), and microcrystalline cellulose (Avicel), were added to a 2.5% alginate system and a one-step gelation of the alginate conducted (no gelatin so two-step gelation was not possible). Table 4 shows that all the added nongelling materials give a weakening of the mechanical properties of the compound gelled matrix.

Evaluation of results from the mass balances and calcium content determinations showed only one compositional parameter which had a specific trend relating its concentration to the measured mechanical properties (Table 5). The water content per unit weight of alginate was observed to increase as the magnitude of the mechanical properties decrease. This may be of significance to the extent that the alginate molecules are the major contributor to the overall texture, and presence of added water can be expected to give added "gel fluidity".

It can be seen that the sucrose-containing gels (AGS, AGSP) decreased greatly in solids content due to sucrose loss and increased in water uptake (due to osmotic transport), giving a sizable reduction in overall percent solids. The sucrose-free samples (AG, AGP) increased in percentage solids primarily due to calcium uptake. The overall mass balances (gel and crosslinking solution) showed that essentially no polymeric species were lost from the gelling systems. This was confirmed for the gelatin by the absence of leached nitrogen in the crosslinking solution.

Analysis of calcium distribution between "bound" and "free" states showed some interesting results, especially if the "bound" calcium can be regarded to be the calcium tied up in the junction zones of the alginate gels. The total calcium uptake was quite variable with the AGSP sample having a very high uptake. However, these differences were related to "free" calcium levels, since all samples had similar "bound" calcium

levels when expressed on an alginate weight basis. This presumably indicates a similar extent of total crosslinking, though the distribution of these junction zones could vary (see Discussion).

Mechancial Properties of Some Fruits

The compression stress-strain behavior of some fruits and a complex fruit simulating alginate gel is shown in Figure 2. While it is recognized that the numerical values of the mechanical parameters of the fruits will vary with variety, maturity, etc., a summary of the mechanical properties of the particular fruits and alginate gel shows that the mechanical parameters of the fruit-simulating alginate gel are in the range of those of the common fruits' (Table 6).

DISCUSSION

Calcium alginate gels are believed to result from the formation of junction zones composed of stacks of alginate molecules with calcium ions packed between the alginate chains (Rees, 1969, 1972). Incorporation of other materials gives calcium alginate gels having different mechanical properties from those of the pure calcium alginate gels. The physical chemistry of multicomponent gel systems is very complex, and, at present, little information is available.

It can be assumed that calcium alginate gels formed in the presence of other materials are still crosslinked frameworks of junction zones of stacked alginate molecules which are basically the same as those present in pure calcium alginate gels. The changed mechanical properties of multicomponent gels may result from:

1. Changes of junction zone size and/or distribution in the gel.
2. Interaction of the non-crosslinked portion of the alginate chains and the incorporated materials.
3. Influence of incorporated materials on moisture content of crosslinked gel.

Addition of materials prior to crosslinking can be viewed as yielding a larger number of widely distributed junction zones, each of a smaller size or junction zones which are concentrated at selected locations in the network.

Changed junction zone size could result from either fewer monomeric units of each alginate molecule participating in junction zone formation or a different number of alginate chains being involved in a given junction zone. The incorporated material could either sterically hinder alginate chain mobility, modify the properties of water molecules or calcium ions, or associate with alginate chains, etc. A uniform and homogeneous distribution of the alginate molecules in the solvent would also favor more, smaller junction zones that are widely distributed throughout the framework of the calcium alginate gel. However, in the two-step procedure used for the gel preparation, a soft gelatin gel was set prior to the crosslinking stop. The molecular arrangements occurring during the setting of the gelatin gel could give a nonuniform distribution of alginate molecules, since it is probable that the alginate molecules are non-uniformly distributed in the highly flexible regions between the widely spaced network links of the gelatin gel.

Before a junction zone can come apart, all of the individual links in the junction zone must be severed simultaneously. Thus, if the incorporation of nongelling material reduces the size of each junction zone, the mechanical strength of the crosslinked calcium alginate would be expected to be weaker by an exponential factor related to the reduction in junction zone size. In addition studies on the mechanical behavior of materials of varying bonding uniformity would indicate that a

calcium alginate gel with uniformly distributed junction zones will have a higher mechanical strength than the calcium alginate gel with an equal number of junction zones nonuniformly distributed since local molecular flow tends to occur more readily with nonuniformly distributed crosslinked network.

Changes associated with junction zones resulting from the presence of added materials should be reflected by changes in the "bound" calcium levels for the various sample compositions. The "bound" calcium content was noted however to remain constant for a variety of components added to the basic alginate-gelatin matrix, indicating that if junction size decreases due to the presence of added species, it is just balanced by an increased number of junction zones. That this behavior would occur for all the species added, and would always result in reduced values of mechanical properties is unlikely. It seems therefore that the action of the added species is not to alter the basic alginate crosslinking.

In addition to interference at the junction zones, there can also be interactions between the noncrosslinked portion of alginate chains and the incorporated materials, or the incorporated materials could influence water uptake in the gel, altering the mobility of the macromolecular components in the gel. It has been noted earlier that the reduction in magnitude of the mechanical properties with addition of sucrose and/or pectin could be related to the increase in water content per unit weight of alginate. No attempt was made to evaluate

the extent to which this additional water was actually available for facilitating alginate chain movement. When the water present in the crosslinked gel is "distributed" over all the solids present, the above-mentioned relationship does not hold, in that the percent total solids does not change in a manner related to the change in mechanical properties. It is, of course, possible that the action of the additional water is to "hydrate" the added solids, which then act as plasticizers in the alginate matrix. This situation is very similar to that existing in cellophane plasticized by hydrophilic plasticizers like glycerol or ethylene glycol which depend for their plasticizing activity on hydration by atmospheric moisture. Sorbitol can have a similar function in chewing gum compositions.

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TABLE 1

MECHANICAL PROPERTIES OF GELATIN AND ALGINATE BASED GELS

		Sample Properties			
		A	B	C	D
	Gelatin	1.5%	1.5%	1.5%	0%
	Alginate	0%	2.5%	2.5%	2.5%
	Crosslinked	No	No	Yes	Yes
Tangent Moduli at Strain (kg/cm^2)	0.3	0.17	0.40	10	4
	0.5	0.44	0.50	23	12
Breaking Strength (kg/cm^2)		0.12	0.19	6.4	5.6
Fracture Energy Density ($kg\text{-}cm/cm^3$)		0.023	0.04	1.0	0.90

TABLE 2

EFFECT OF SUCROSE ON THE MECHANICAL PROPERTIES OF SOME GELS

Gel Composition[a]	N[b]	Breaking Strength (kg/cm^2)	Fracture Energy Density ($kg\text{-}cm/cm^3$)
A	11	5.45 ± 0.15	0.923 ± 0.016
AS	11	3.64 ± 0.18	0.814 ± 0.026
AG	11	6.01 ± 0.18	1.045 ± 0.036
AGS	9	2.85 ± 0.27	0.571 ± 0.011
AG(P-L)	9	1.99 ± 0.21	0.413 ± 0.028
AG(P-L)S	9	1.03 ± 0.06	0.262 ± 0.015
AG(P-H)	8	1.34 ± 0.05	0.395 ± 0.008
AG(P-H)S	10	0.65 ± 0.04	0.246 ± 0.013

a. A = Alginate (2.5%)
S = Sucrose (30%)
G = Gelatin (1.5%)
P = Pectin (2%) (L, H: Low or High Level of Esterification)

b. Number of samples

TABLE 3

EFFECT OF PECTIN AND ITS LEVEL OF ESTERIFICATION ON THE MECHANICAL PROPERTIES OF THE GELS

Gel Composition	N[b]	Breaking Strength (kg/cm^2)	Fracture Energy Density ($kg\text{-}cm/cm^3$)
A	11	5.45 ± 0.15	0.923 ± 0.016
A(P-L;1.0%)	10	3.40 ± 0.16	0.546 ± 0.036
A(P-L;2.0%)	10	3.30 ± 0.10	0.535 ± 0.020
A(P-H;2.0%)	8	1.54 ± 0.17	0.256 ± 0.011
A(P-H;3.0%)	9	1.09 ± 0.10	0.203 ± 0.015
AG	11	6.01 ± 0.18	1.405 ± 0.036
AG(P-L;2.0%)	9	1.99 ± 0.21	0.413 ± 0.028
AG(P-H;2.0%)	8	1.34 ± 0.05	0.395 ± 0.008
AGS	9	2.85 ± 0.27	0.571 ± 0.011
AG(P-L;2.0%)S	9	1.03 ± 0.06	0.262 ± 0.015
AG(P-H;2.0%)S	10	0.65 ± 0.04	0.246 ± 0.013
2.0% P-L	5	0.88 ± 0.07	0.195 ± 0.011

a. A = Alginate (2.5%)
S = Sucrose (30%)
G = Gelatin (1.5%)
P = Pectin (L, H = Low or High level of Esterification)

b. Number of samples

TABLE 4

EFFECT OF SOME POLYMERIC AND NONPOLYMERIC MATERIALS ON THE MECHANICAL PROPERTIES OF CALCIUM ALGINATE GELS

Gel Composition[a]	N[b]	Breaking Strength (kg/cm^2)	Fracture Energy Density ($kg\text{-}cm/cm^3$)
A	11	5.45 ± 0.15	0.923 ± 0.016
A, PVA 0.5%	10	2.05 ± 0.23	0.435 ± 0.011
A, PVA 1.0%	10	2.46 ± 0.28	0.469 ± 0.020
A, PVA 2.0%	12	2.67 ± 0.15	0.488 ± 0.023
A, CMC 0.5%	10	1.75 ± 0.06	0.334 ± 0.006
A, CMC 1.0%	10	1.83 ± 0.10	0.317 ± 0.008
A, CMC 2.0%	10	0.97 ± 0.04	0.174 ± 0.004
A, avicel 1%	11	3.79 ± 0.24	0.584 ± 0.012
A, avicel 2%	11	3.88 ± 0.30	0.650 ± 0.021
A, lysine 0.5%	10	3.14 ± 0.22	0.598 ± 0.039
A, lysine 1.0%	10	3.74 ± 0.19	0.666 ± 0.036

a. A = Alginate
PVA = Polyvinyl alcohol
CMC = Carboxymethylcellulose

b. Number of samples

TABLE 5

COMPOSITION OF ALGINATE GELLING SYSTEMS BEFORE

AND AFTER CROSSLINKING AND SOME RESPECTIVE MECHANICAL PROPERTIES

Gel Composition[a]	Solids (g)		Water (g)		% Solids		$\frac{gmH_2O}{g\ alginate}$	Calcium mg/g alginate			Breaking Strength (kg/cm^2)	Fracture Energy ($kg\text{-}cm/cm^3$)
	Before	After	Before	After	Before	After	After	Total	Bound	Free		
A	1.22	2.18	53.14	33.08	2.25	6.18	27.11	202	84	118	5.45	0.923
AG	2.00	2.93	48.68	40.60	3.95	6.73	36.50	189	81	109	6.01	1.045
AGS	13.58	5.79	38.36	42.77	26.1	11.9	43.43	281	85	196	2.85	0.571
AGP	2.79	3.62	46.53	49.48	5.66	6.82	46.35	194	83	111	1.99	0.413
AGSP	14.14	7.21	37.37	55.33	27.5	11.5	57.24	369	97	272	1.03	0.262

a. A = Alginate
G = Gelatin
S = Sucrose
P = Pectin (High level of Esterification)

TABLE 6

MECHANICAL PROPERTIES OF SOME FRUITS AND A FRUIT-SIMULATING ALGINATE GEL

Item	Tangent Modulus (kg/cm^2)	Breaking Strength (kg/cm^2)	Fracture Energy Density ($kg\text{-}cm/cm^3$)
Banana	1.31	0.30	5.9×10^{-2}
Peach	2.06	0.28	4.5×10^{-2}
Apple	12.83	2.39	29.6×10^{-2}
Fruit-Simulating Alginate Gel[a]	0.95	0.65	25×10^{-2}

a) Fruit-Simulating Alginate Gel (in g/100ml prior to crosslinking)
Alginate (2.5)
Gelatin (1.5)
Pectin (2.0) (High degree of esterification)
Sucrose (30)

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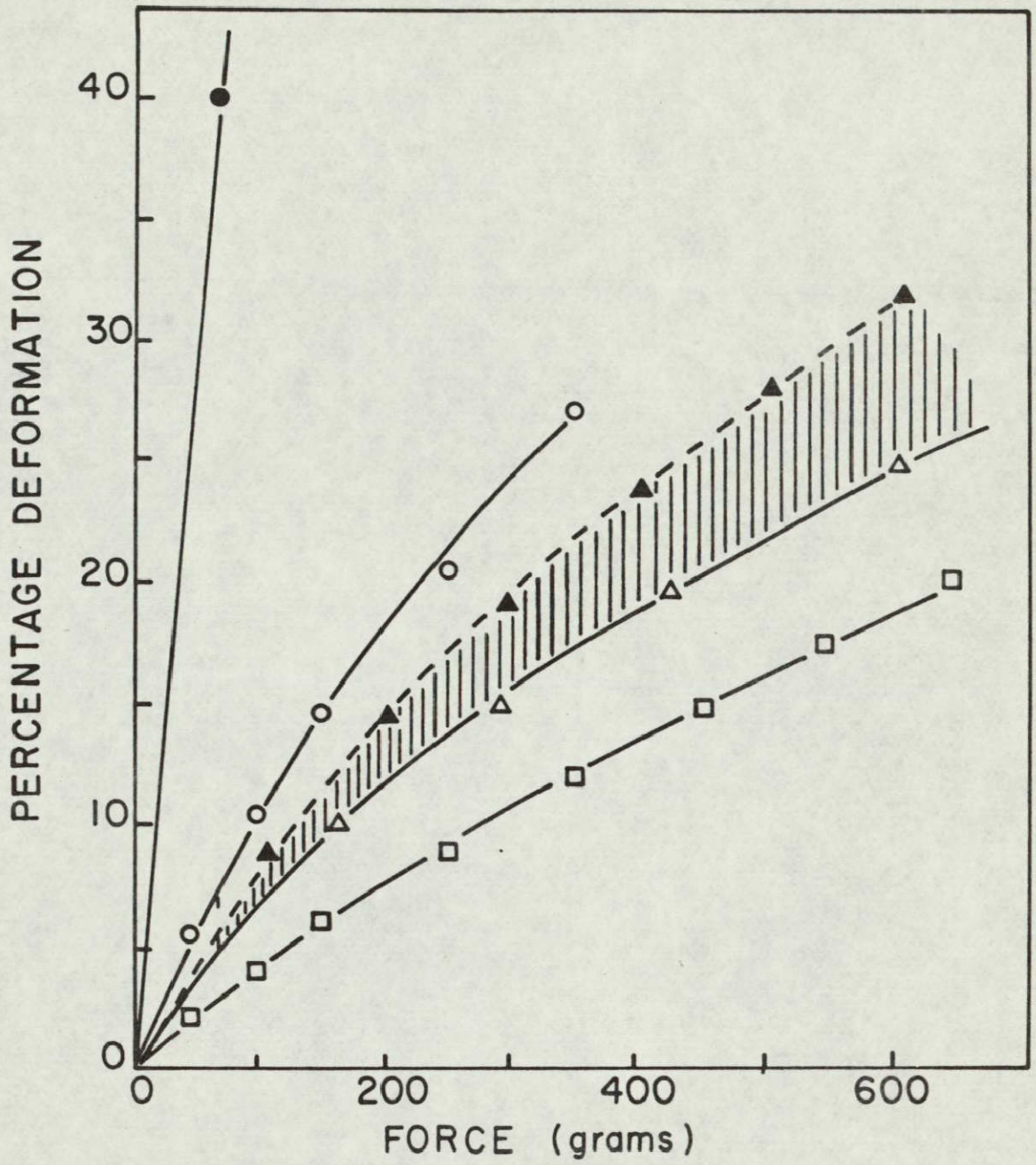
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20
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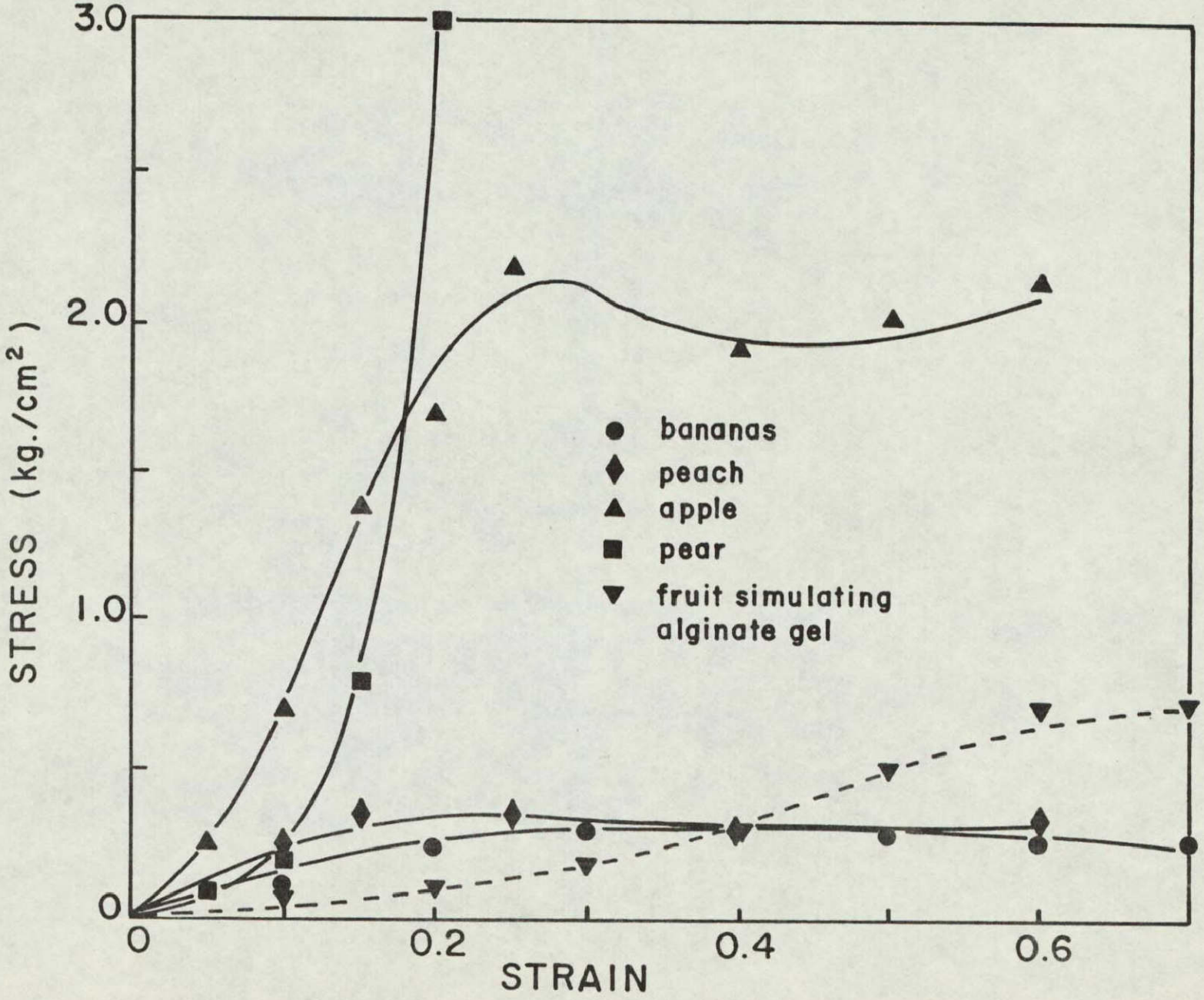
200
400
600
FORCE (grams)


3.0
2.0
1.0
0
STRESS (kg./cm²)
0
0.2
0.4
0.6
STRAIN
bananas
peach
apple
pear
fruit simulating alginate gel

4.4 Cross-linking Behavior of Alginate Gels

In the production of the artificial food matrices, the thermally set alginate-containing gelatin gel is placed in a cross-linking solution containing a source of calcium ions so that the alginate molecules can form the stable junction zones which give the artificial food matrices their desirable texture. In our studies calcium lactate as a 4.5 percent solution was used as the source of calcium ions. Although the rate of the diffusion of calcium ions was noted in our earlier work (Luh et al., 1976, J. Fd. Sci. 41:89-93) in terms of the formation of cross-linked gel, it was not known to what extent the diffusing calcium was taking part in the formation of the gel network.

Initial studies were conducted using the formulation giving artificial food matrices of best textural quality, 2.5% alginate, 2.0% pectin, 1.5% gelatin, and 30% sucrose. Changes in total solids and moisture content during the cross-linking in the calcium lactate solution were monitored. It was noted that in cross-linking a sizable amount of solids is lost, presumably sucrose, and that much water is taken up by the gel solution. The solids and water contents at various times in the process follow.

Table 1

Time (hrs)	g. H_2O / g. init. wet gel	g. solids / g. init. wet gel	% solids
0	0.73	0.27	27
1.5	0.98	0.20	17
6.5	1.06	0.16	13
11.5	1.06	0.15	12
24	1.04	0.12	10

Both the uptake of calcium by the gelling sample and the loss of calcium from the calcium lactate solution were determined by means of the AOAC method of calcium analysis with EDTA titration. The results below show that the mass balance was extremely good and that the uptake of calcium by the gel was rapid over the initial 1.5-hour period, was still sizable over the next five hours, and then was essentially constant, presumably signifying the end of cross-linking and equilibration of the fluid phase in the gel with the calcium lactate bath.

Table 2

Time (hrs)	Ca uptake by gel (mg)	Ca lost from solution (mg)	$\frac{\text{Ca uptake}}{\text{Ca loss}}$	$\frac{\text{Ca in gel}}{\text{initial gel solids}}$ (mg/g)
0	0	0		0
1.5	190	188	1.01	15.76
6.5	292	286	1.02	21.41
11.5	308	299	1.03	22.61
24	317	314	1.01	24.83

These studies continued with analysis of the uptake of calcium ions by the gelling samples and the distribution of calcium between structure forming elements and nonstructurally related areas. The following procedure was used to obtain the preceding data as well as the data in the following experiments involved in calcium analysis:

A. Preparation of Sample for Calcium Mass Balance

1. Gels of defined composition were prepared and refrigerated 24 hours at 4°C.

2. Set gel was cut into approximately 1 cm cubes. Fifty grams were weighed into a preweighed screw cap jar (with rubber seal to prevent evaporation losses) containing 200 ml of a 4.5 percent calcium lactate solution. All weights of all materials were recorded at each step of procedure.

3. A portion of uncross-linked gel was weighed and set aside for freeze-drying to determine the original moisture content of the gel.

4. Gels were cross-linked in solution for 24 hours at 4°C.

5. After cross-linking, gels were removed from the solution and weighed after carefully draining excess calcium lactate solution; solution was also weighed to determine change in weight during cross-linking. In some experiments cross-linked gels were either boiled for 10 minutes or soaked for 24 hours in water to determine the

amount of calcium ion leached out of the gel. For boiling the cross-linked gel was weighed and placed in a screw cap jar with 200 ml of boiling water. (The jar was vented to allow for expansion during heating.) For soaking 24 hours in distilled water, the setup was similar to the cross-linking step except the gels were gently agitated at room temperature. Analyses for calcium in gels and solution were performed similarly.

6. Cross-linked gels were freeze-dried to determine moisture contents.

7. A volumetric portion (10 ml) of the cross-linking solution (before and after) was weighed and freeze-dried to determine the solids content.

B. Analysis of the Calcium in Cross-linking Solution

1. A volumetric portion of the calcium lactate solutions (before and after cross-linking) was analyzed for calcium by titration with EDTA according to the AOAC method for analysis of calcium using Eriochrome Black T as an indicator.

C. Analysis of Calcium in the Gel

For Total Calcium Determination

1. 1.20 g of pulverized freeze-dried gel were ashed in crucibles for 4.5 hours at 525°C.

2. After cooling sample, concentrated HCl (6 N) was added dropwise until no further reaction was noted. (A violent fizzing reaction occurs between CaO and HCl.)

3. The sample was carefully transferred to a 100 ml volumetric flask and diluted to volume with distilled water.

4. An aliquot of sample was titrated with EDTA to determine the calcium content.

For Analysis of "Unbound" Calcium

1. 1.20 g of pulverized freeze-dried gel were put into a 100 ml volumetric flask. Only about 75 ml of distilled water were added to allow room for agitation.

2. Samples were shaken for 24 hours; they were then diluted to volume with distilled water.

3. Samples were filtered by suction through coarse filter paper (No. 589 Black Ribbon).

4. A volumetric portion of the clear filtrate is analyzed by titration with EDTA for calcium.

The distribution of the calcium has been determined by assuming that calcium ions that are involved in structural cross-links are not removable by a leaching process. Calcium ions which exist in the bulk gel without involvement in the alginate junction regions were assumed to be removable by leaching of the gel in water for 24 hours. This calcium fraction is called "free" calcium. Gel samples which were held for various times in the cross-linking bath were analyzed for total calcium content. Some gels were placed in water at room temperature for 24 hours, and the calcium which leached into the water, measured. Bound calcium was determined by the

difference of the total calcium and the amount leached. The calcium contents have been expressed on a unit alginate basis since this component is assumed to remain in the gel under all test conditions. It was noted that the bound (structure related) calcium appeared to reach a near equilibrium value quickly (within 1.5 hours, Table 3). The free calcium, however, continued to increase.

These studies were expanded to include evaluation of the influence of the system composition on calcium distribution and solids lost in cross-linking. In all cases the overall mass balances on total solids, total calcium, and water were very good. One study also analyzed the bound calcium in gel samples after the 24-hour leaching period and compared the measured values to those calculated by the difference of total calcium and free calcium. Again, good agreement was obtained. The results of these studies of distribution of calcium between bound (structure-forming) and free (nonstructural) conditions are shown in Table 4. It can be seen that in all cases the level of bound calcium is very similar and that the secondary treatments of either soaking 24 hours in distilled water or 10 minutes in boiling water had no effect on the bound calcium. The level of uptake of total calcium was much higher for the AGSP samples than for the other three compositions; the difference was exclusively because of increased uptake of free calcium. Soaking the samples gave a sizable

reduction of the free calcium levels for all samples, although there appeared to be some residual free calcium as measured by the testing procedure even for samples soaked for 24 hours. (In the test the gel, after the soaking treatment, was freeze-dried, pulverized, re-extracted, and the extract analyzed for free calcium. The calcium remaining in the gel after this pulverization and extraction is "bound" calcium.)

Studies on the gross transport of solids and water are summarized in Tables 5 and 6 where the changes in solids content, water content, and percent solids for the cross-linking and soaking steps are given. It is noted that percentage solids (Table 6) can change because of transport of either solids and/or water. Very little net change is associated with the AG or AGP gels since they have no easily diffusible species. In these gels the increase in absolute solids is associated with calcium uptake, whereas the major component of the increase of percent solids is because of loss of water (Table 5). The sucrose containing gels undergo continual sizable loss of solids because of loss of sucrose. Note that after the 24-hour cross-linking the sugar-containing gels still have a higher percentage solids but that after the secondary soaking all the gels have about the same percentage solids. This indicates that sucrose can diffuse easily out of the cross-linked gel.

Several studies on the effect of system composition on the extent of cross-linking as measured by calcium ion binding were undertaken. In an alginate-gelatin gel results obtained

C-2

with four different initial concentrations of alginate (at constant gelatin concentration) indicate that the amount of bound calcium per gram of alginate remains constant after cross-linking 24 hours in 4.5 percent calcium lactate (Table 7). The amount of free calcium seems to decrease with increasing alginate concentration; probably because of the more dense, compact texture obtained with higher alginate concentrations, there are less open voids for free calcium to deposit.

Tests were conducted to determine the validity of measuring bound calcium by differences instead of by direct analysis of the calcium level of the extracted gels. Examination of data from studies on the effect of alginate concentration on extent of calcium binding have shown that determinations based on measuring the differences between "total calcium" and free calcium" were equal to those based on direct analysis of the water extracted gels by ashing and titration of the dissolved ash (Table 8). Thus, in most cases difference measurements were generally used since they are simpler to conduct, although direct analysis was conducted periodically as a control.

A study on the extent of calcium ion binding by alginate in a pure alginate system was conducted with a slight variation in procedure. In this case the two-step gelling procedure which requires gelatin to give the initial matrix

cannot be used, and instead a 2.5 percent alginate solution was placed as drops into the cross-linking bath. This resulted in a slightly different geometry (spheres) than that obtained using the two-step gelation (cubes). Results from this test showed that the level of calcium ion bound was similar to samples in which the alginate was present initially in the gelatin stabilized matrix (Table 9).

Test systems were prepared in which the gelatin or pectin concentration was varied. The results of these tests, which are given in Tables 9 and 10, indicate that the extent of calcium ion binding by the alginate molecules is essentially independent of the system gelatin or pectin concentrations over the range studied. Again it is seen that the free calcium level changes with system composition, though in this case it increased with increase in the contents of either gelatin or pectin. The free calcium concentration remained relatively constant for the lower initial pectin concentrations but then showed a sizable increase at the higher pectin concentrations. This could indicate a weak pectin-calcium ion interaction when the pectin concentration levels are sufficiently high to allow pectin molecules to interact.

Studies on the influence of calcium ion concentration in the cross-linking bath on the extent of calcium binding by the alginate-gelatin system show that except for the lowest concentration tested, the level of calcium binding is constant (Table 11). At the lowest concentration (0.5 g/100 g H_2O)

the amount of bound calcium was somewhat lower which is indicative of a reduced level of cross-linking. The free calcium levels were directly related to the solution concentration. It was noted above that over the range of concentrations tested, the extent of calcium ion binding per unit weight of alginate in the various matrix systems examined was independent of:

1) initial alginate concentration
2) initial gelatin concentration
3) initial pectin concentration

It was also noted that pure alginate binds calcium to the same extent as the food matrices of more complex composition. Free calcium levels were subject to variation with concentration of added component, decreasing with increasing alginate, remaining unchanged with increasing gelatin, and increasing with increasing pectin. These results could indicate that the total binding sites on the alginate are being measured. To evaluate if this "bound" calcium (which is defined as bound by the water extraction step) reflects the total sites for binding calcium rather than those related to cross-links, studies were initiated to determine if the "bound" calcium consists of two states, calcium in cross-links and calcium bound on sites on single molecules (i.e. no cross-links). The ability of NaCl or HCl to replace calcium at the alginate sites by mass action relationships was used as a measure of the interchangeability of calcium ions.

The effect of HCl concentration on the extraction of calcium from an alginate-gelatin gel system is shown in Figure 1 and Table 12. At low concentrations, below 10^{-3}N, the acid solution has effects identical to pure water extraction. There appears to be an intermediate range of concentrations (10^{-3} to 10^{-1}N) in which there is a sharp increase in calcium extraction. Concentrations above 10^{-1}N remove all the calcium from the gel in the first extraction. A second extraction in the intermediate range of HCl concentrations shows an increased amount of calcium removed over the first extraction. At concentrations below 10^{-3}N a second extraction has little or no effect. Figure 2 shows the effect of NaCl concentrations on the extraction of calcium from an alginate-gelatin gel system. For NaCl concentrations ranging from 5-20 percent w/v, the level of unextracted calcium gradually decreases. Between 0 and 5 percent NaCl there is a fairly sharp decrease in unextracted calcium; however, there are no intermediary values to obtain an accurate curve. A second extraction shows an increased amount of calcium removed over the first as noted above for the HCl extractions. During the extraction procedure with NaCl, there was considerable swelling of the gel resulting in much more viscous solutions making separation of solid and liquid phases more difficult.

It appears on the basis of these results that differing extractive capabilities exist for NaCl and HCl with the HCl

giving complete removal of calcium at levels above 10^{-1}N. If it can be assumed that significant bond energy differences exist between cross-link bound calcium and single site bound calcium, the results found above would indicate that calcium binding is occurring only in cross-links since no intermediate levels of unextracted calcium were found for the HCl extractions. (Mass balances on calcium ion distribution between gel and solution indicate that the analysis technique for total calcium will show calcium in cross-links, and thus the zero level found for HCl extractions is a real zero level.) The results for NaCl extractions are a little more confusing since they do not reach the zero level, but this may reflect the limited concentration range available for study because of the approach of the solubility limit for NaCl in water.

The continuum for decrease of unextracted calcium over the HCl concentration range of 10^{-3} to 10^{-1}N can indicate that bonding energy in cross-links is not uniform but may have a distribution of energies. While it is difficult to specify for sure, since the gels are extracted in the ground state, it seems that gel structure is lost when the unextractable calcium level reaches 0. With NaCl extractions some structure seems to remain, but results are limited. While some information has been developed in this area, much more work is needed to better understand the cross-linking behavior in the complex gel systems with which we have been working.

Table 3: Time Dependence of Distribution of Calcium in Alginate Gel System

Time (Hrs.)	Calcium		(Mg Calcium / g Alginate)
	Total	Bound	Free
1.5	230	85	146
6.5	314	88	224
11.5	331	89	242
24	363	91	272

Table 4: Effect of Composition on Distribution of Calcium in Alginate Based Gelling Systems

Sample [a]	Process [b]	Calcium $\left(\frac{\text{mg Calcium}}{\text{g Alginate}}\right)$		
		Total	Bound	Free
AG	XL	189	81	109
AG	XL + Boil	115	81	34
AGP	XL	194	83	111
AGP	XL + Boil	128	83	45
AGSP	XL	369	97	272
AGSP	XL + Boil	198	95	103
AGS	XL	281	85	196
AGS	XL + Boil	146	87	59
AGSP	XL	343	94	250
AGSP	XL + Soak	154	92	62
AGP	XL	261	96	165
AGP	XL + Soak	144	100	44

a A: Alginate
S: Sucrose
G: Gelatin
P: Pectin

b XL: in cross-linking bath (4.5% Ca) for 24 hours
BOIL: in boiling water for 10 minutes
SOAK: in distilled water for 24 hours

Table 5: Changes in Solids and Water Contents for Treatments of Alginate Gels [a]

Sample [b]	Initial Gel		After Cross-linking		After Cross-linking and Soaking	
	Solids	Water	Solids	Water	Solids	Water
AG Boil	2.00	48.68	2.93	40.60	2.13	33.75
Soak	1.99	47.91	2.77	40.34	2.04	31.90
AGP Boil	2.79	46.53	3.62	49.48	2.85	47.74
Soak	2.88	47.06	3.95	49.95	2.97	50.46
AGSP Boil	14.14	37.37	7.21	55.33	4.07	56.18
Soak	15.81	39.68	8.06	58.82	3.38	56.50
AGS Boil	13.58	38.36	5.79	42.77	3.12	37.39
Soak	13.94	38.98	6.39	43.80	2.15	31.49

a) All values in grams

b) Sample Codes given on Table 2

Table 6: Change in Percentage Solids of Alginate Gels Due to Net Transport of Solids and Water

Sample [a]	Percentage Solids		
	Initial	After Cross-linking	After Cross-linking and Soaking
AG Boil	3.95	6.73	5.93
AG Soak	3.99	6.43	6.01
AGP Boil	5.66	6.82	5.63
Soak	5.77	7.33	5.56
AGSP Boil	27.5	11.5	6.76
Soak	28.5	12.1	5.65
AGS Boil	26.1	11.9	7.70
Soak	26.3	12.7	6.38

a) Sample Codes given on Table 2

Table 7

EFFECT OF INITIAL ALGINATE CONCENTRATION ON

FREE AND BOUND CALCIUM IN CROSS-LINKED GELS

(Initial gelatin concentration was constant at 2g/100g H_2O)

Initial Alginate Concentration (g/100g H_2O)	Total Solids (%)		Calcium Content After Cross-linking mg/g alginate		
	Before Cross-linking	After Cross-linking	Total Calcium	Free Calcium	Bound Calcium
0[a]	1.83	4.03	207	207	0
2.0	3.56	6.68	218	138	80
2.5	3.90	7.85	210	131	79
3.0	4.40	7.96	191	110	81
3.5	4.82	8.60	173	93	80

[a]Calcium contents based on mg calcium/g gelatin

Table 8

Comparison of Two Methods to Determine Bound Calcium in Cross-linked Gels with Different Initial Alginate Concentrations (Initial gelatin concentration was constant at 2.0g/100g H_2O)

Initial Alginate Concentration (g/100g H_2O)	Bound Calcium (mg/g. alginate) Difference[a]	Direct Analysis[b]
2.0	80	78
2.5	79	81
3.0	81	80
3.5	80	80

a. determined by calculation of difference between "total calcium" and "free calcium"
b. determined by ashing and analyzing precipitate after aqueous extraction for "bound calcium"

Table 9

EFFECT ON INITIAL GELATIN CONCENTRATION ON

FREE AND BOUND CALCIUM IN CROSS-LINKED GELS

(Initial alginate concentration was constant at 2.5g/100g H_2O)

Initial Gelatin Concentration (g/100g H_2O)	Total Solids (%)		Calcium Content After Cross-linking mg/g alginate		
	Before Cross-linking	After Cross-linking	Total Calcium	Free Calcium	Bound Calcium
0	2.25	6.18	202	118	84
1.0	3.08	6.70	210	125	85
1.5	3.41	7.10	211	126	85
2.0	3.88	7.85	225	138	87
2.5	4.32	8.05	222	138	84
3.0	4.73	8.25	222	137	85

Table 10

EFFECT OF INITIAL PECTIN CONCENTRATION ON

FREE AND BOUND CALCIUM IN CROSS-LINKED GELS

(Initial gelatin concentration was constant at 2.0g/100g H_2O
Initial alginate concentration was constant at 2.5g/100g H_2O)

Initial Pectin Concentration (g/100g H_2O)	Total Solids (%)		Calcium Content After Cross-linking mg/g alginate		
	Before Cross-linking	After Cross-linking	Total Calcium	Free Calcium	Bound Calcium
0	3.88	7.85	225	138	87
1.0	4.87	6.90	231	137	95
1.5	5.18	7.09	237	138	99
2.0	5.75	7.21	251	159	92
2.5	5.86	7.51	252	166	86
3.0	6.47	7.91	292	205	88

Table 11

Effect of Initial Calcium Lactate Concentration on Free and Bound Calcium in Cross-linked Gels (Initial gelatin concentration was constant at 2.0g/100g. H_2O Initial alginate concentration was constant at 2.5g.[a]/100g. H_2O)

Initial Calcium lactate Concentration (g/100g H_2O)	% Total Solids Before Cross-linking	% Total Solids After Cross-linking	Calcium Content After Cross-linking (mg/g. dry alginate[a]) Total Calcium	Free Calcium	Bound Calcium
0.5	4.29	3.43	75	7	68
1.0	4.29	4.91	104	18	86
2.0	4.29	6.11	136	46	90
3.0	4.29	6.78	171	80	91

a. Alginate was vacuum dried 24 hrs. at 50°C
M.C. from jar = 11.3g/100g dry alginate

Table 12

EFFECT OF HCl EXTRACTION ON BOUND CALCIUM IN CROSS-LINKED GELS

(Initial gelatin concentration was constant at 2.0g/100g H_2O)
(Initial alginate concentration was constant at 2.5 g/100g H_2O)

Concentration of HCl Extracting Solution	Extractable Calcium (mg/g dry alginate)		Unextractable Calcium (mg/g dry alginate)	
	1st extract[a]	2nd extract[b]	1st extract[b]	2nd extract[a]
	Total extracted			
0 (pure H_2O)	128	130	87	85
0.0001 N	127	130	88	85
0.001 N	129	132	86	83
0.004 N	135	145	80	70
0.006 N	134	153	81	62
0.008 N	136	161	79	54
0.01 N	136	163	79	52
0.02 N	148	201	67	14
0.04 N	178	212	37	3
0.06 N	212	215	3	0
0.10 N	217	215	0	0
0.20 N	213	215	2	0
0.50 N	216	215	0	0
1.0 N		215		0

a. Calcium values determined by direct analysis

b. Calcium values calculated by difference - total calcium in unextracted gel = 2.5 mg/g dry alginate

Figure 1. Concentration of HCl extracting solution versus remaining unextracted calcium in gel for first and second extractions.

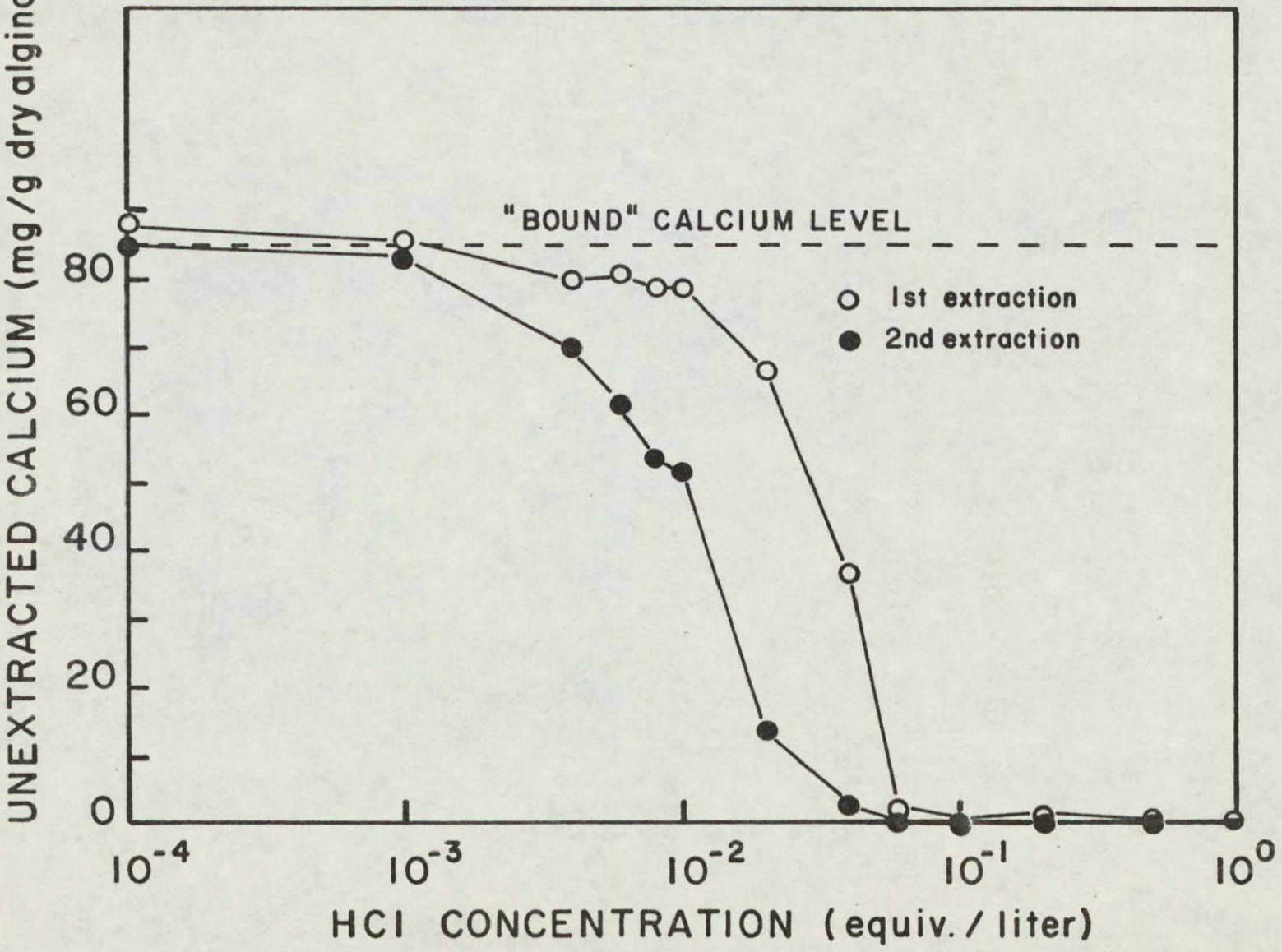
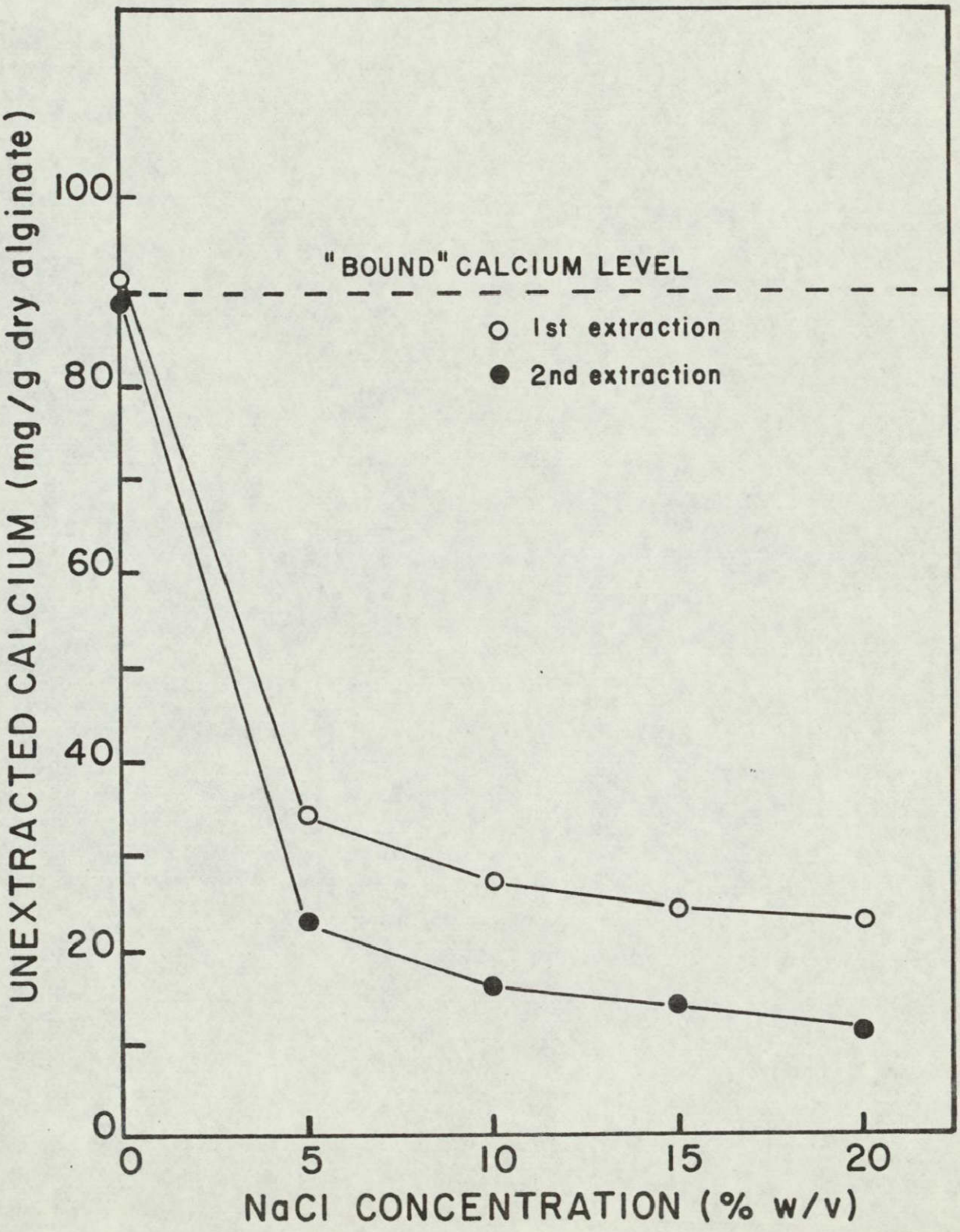


Figure 2. Concentration of NaCl extracting solution versus remaining unextracted calcium in gel for first and second extractions.



4.5 Incorporation of Ascorbic Acid into AFM

Studies on the incorporation of ascorbic acid into the artificial food matrix have continued with evaluation of methods for analyzing the ascorbic acid content of the gelled material. It was noted that extraction of the artificial food matrices resulted in incomplete recovery of added ascorbic acid. It was not possible to determine if this was because of incomplete recovery in the extraction process or loss of ascorbic acid in the gelation process. Efforts to macerate the gel in the wet state did not give significantly improved recoveries of ascorbic acid (about 40 percent of theoretical). However, if the gel was first freeze-dried and then ground in the dry state prior to extraction, good recovery (about 85 percent of theoretical) of ascorbic acid was found. Approximately 1 gram of ground gel is mixed with 10 ml of water and allowed to sit for 10 minutes. Fifteen (15) ml of extraction solution was added and the mixture homogenized in a high speed mixer. Aliquots of the liquid phase are analyzed for ascorbic acid.

The artificial food matrix system is a complex multicomponent material. Tests were conducted to determine if any chemical species present at the various steps of the process would interfere with the ascorbic acid analysis using indophenol titration. These tests were conducted over a 48-hour holding period since in some cases (especially with the calcium lactate cross-linking) long time stability is quite important. The

results shown in Table 13 indicate that the matrix components do not interfere with the ascorbic acid analysis. The ascorbic acid is stable in the calcium lactate cross-linking bath when held covered at refrigeration temperatures. The loss of ascorbic acid at room temperature is higher at the more extended periods of time. However, if artificial food matrix piece size is chosen so that cross-linking times of less than 24 hours are suitable, then the loss of ascorbic acid will not be too severe.

There also was no loss of ascorbic acid over a 2-hour period in a sucrose solution as used for the osmotic concentration of the gelled systems prior to freeze drying.

	Ascorbic Acid (mg/ml)	
% Added	0 hrs.	2 hrs.
0.25	2.8	2.76
0.50	5.5	5.3

These results indicate that losses of ascorbic acid will not be severe for the cross-linking or osmosis concentration steps, especially if these steps are conducted in closed containers or at reduced temperatures.

Table 13

Determination of Ascorbic Acid in the Presence of Components of the Artificial Food Matrix

Component	Initial Ascorbic Acid (%)	Ascorbic Acid Content (mg/ml) 0 hrs.	5 hrs.	24 hrs.	48 hrs.
Gelatin (1.5% w/v)	0.5	5.25	4.65	5.05	4.96
Pectin (2.0% w/v)	0.5	4.98	4.94	5.16	4.94
Pectin + Gelatin	0.5	5.42	5.18	5.46	5.04
Calcium Lactate					
Refrig.; covered	0.1	1.11	1.11	0.99	0.94
	0.3	3.20	3.37	2.92	2.97
	0.5	5.50	5.67	5.02	5.05
Room temp.; covered	0.1	1.03	1.09	0.88	0.72
	0.3	3.3	3.27	2.90	2.79
	0.5	5.67	5.57	4.70	4.23
Room temp.; open	0.1	1.12	1.08	0.79	0.57
	0.3	3.27	3.25	2.88	2.90
	0.5	5.62	5.47	4.75	4.31

4.6 Production of Freeze-dried Products Incorporating AFM

Two products with simulated fruit gels incorporated in a pudding matrix were prepared and sent to NASA/JSC in accordance with the provisions of the contract. One product was prepared using powdered nonfat dry milk; the other product was prepared with whole milk. The following processing criteria were used in the preparation of these two products:

A. Preparation of Nonfat Dry Milk Vanilla Pudding with Freeze-dried Orange-flavored Gel Pieces (Product A)

1. Per one package (106 g.) of commercial brand Jell-O Vanilla Instant Pudding and Pie Filling 48.25 g Carnation Instant Nonfat Dry Milk (N.F.D.M.) and 20 g freeze-dried orange-flavored gels* were added and mixed together.

2. To rehydrate Product A, 2.6 g water were added per 1.0 g dry mix and then blended thoroughly for two minutes; it was then refrigerated for about one hour. (Length of time at refrigerated temperatures determines the texture of the gel pieces, the longer the time, the softer the gel.)

B. Preparation of Freeze-dried Whole Milk Vanilla Pudding with Orange-flavored Gel Pieces (Product B)**

1. Per one package (106 g.) of Jell-O Vanilla Instant Pudding and Pie Filling 65 g wet gels* (before freeze-drying) and 473 ml whole milk were added and mixed together thoroughly for two minutes, refrigerated for 15 minutes, frozen slowly at -20°C and freeze-dried.

2. To rehydrate Product B, 2.6 g water were added per

1.0 g dry mix, blended thoroughly, and refrigerated for about one hour.

**The preparation of Product B for the organoleptic evaluation in Test No. 3 (Table 14) was prepared as described above. This product when freeze-dried took the form of a dense cake-like structure making rehydration slightly difficult. Gelation of the starches would start before complete rehydration (even with constant stirring) forming small lumps in the pudding matrix. For the final product sent to NASA/JSC, the following changes in the preparation were made. To facilitate rehydration of the pudding matrix, the pudding was prepared as directed on the back of the package (106 g mix/473 ml whole milk), freeze-dried without adding gel pieces, and comminuted to a powder with a Waring blender. Per 150 grams of powdered freeze-dried pudding, 20 g dry gel were added. Rehydration of this powdered product with the appropriate quantity of water was much more successful because of complete absorption of water prior to the onset of gelation, thus forming a smoother texture without lumping.

*C. Preparation of Simulated Orange-flavored Fruit Gels

1. Basic formula: (based on 100 g water)

30 g.	sucrose
1.5 g.	gelatin
2.0 g.	pectin
2.5 g.	alginate
1 ml	Givauden orange juice flavor F-4569

2. Gelatin and sucrose were dissolved in water with heat.

3. Pectin, alginate, and flavoring were added and homogenized in a Waring blender for 30 seconds.

4. Gel mixture was poured into container of sufficient size to allow a 0.5 cm-thick layer to be formed. Mixture was set in four hours at 4°C.

5. The gels were cut into small pieces (roughly 0.5 cm^3) and cross-linked in an excess of 4.5 percent calcium lactate solution for 24 hours.

6. Gel pieces were rinsed with distilled water to remove any adhering calcium lactate and osmosed in a 50 percent sucrose solution for two hours; they were then rinsed to remove excess surface sucrose and then ready for freeze-drying.

7. Artificial coloring was added during the cross-linking and osmosis steps. A commercial brand food color by Durkee was used.

Organoleptic evaluations were conducted on these rehydrated products. Average test scores are reported in Table 14. Test No. 1 compares different methods of preparation of the pudding matrix without the addition of gel pieces. Since the product is designed for use in space travel, the methodology involved in preparation of the product for serving is of great importance. According to the directions on the commercial brand Jell-O Vanilla Instant Pudding and Pie Filling, the contents (which are in powdered form) should be rehydrated

with whole milk and beaten for two minutes. Because this method is obviously inconvenient on a space flight, investigation of an alternative method was made. An organoleptic evaluation comparing the following samples was made:

1. Pudding mix prepared as directed on back of container using whole milk and beaten.
2. Pudding mix prepared similarly except substituting N.F.D.M. for whole milk.
3. Pudding mix prepared with N.F.D.M. and stirred without beating.

As can be seen in Table 14, test scores for taste of all samples are high. The texture of the products made with N.F.D.M., although not rated as highly as the one with whole milk, is still quite acceptable. No noticeable differences between textures of the samples with beating and stirring were observed.

Test No. 2 gives a comparison between:

1. Sample prepared with whole milk and orange-flavored gel pieces.
2. Sample prepared with N.F.D.M. and orange-flavored gel pieces.

In the preparation incorporating the orange-flavored gel pieces in the pudding matrix, the test scores remained good with no significant overall differences between the two products (Table 14). In each of the above tests (Nos. 1 and 2) samples prepared with whole milk were rated slightly

higher than those prepared with N.F.D.M. Comments showed that the whole milk product was more creamy and had a better consistency than the N.F.D.M. sample. It was then decided to try to make a product with whole milk and freeze-dry it so that it could simply be rehydrated with water.

Test No. 3 compares:

1. Sample prepared fresh with whole milk and freeze-dried gels.
2. Sample prepared with whole milk and gels, freeze-dried together, and rehydrated.

Both samples as shown in Table 14 had high scores without any significant difference between them.

Shelf life of Product A in the dry state should be highly acceptable. All the ingredients with the exception of the orange pieces are commercial products with good storage stability. A preliminary storage study was made with artificially orange-flavored gels when incorporated in yogurt.[1] No deterioration was observable after two months of storage at room temperature (23°C) in darkness in sealed jars under air. The shelf life of Product B with whole milk, however, is not well-established; therefore, a short term storage stability test was carried out on the evaluation of freeze-dried whole milk pudding with orange-flavored gel pieces.

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[1]Annual Report Phase III, Pages 4-20
NASA/JSC Contract No. 9-12485

Samples were stored for 5 weeks at 23°C (room temperature) in sealed cans in air or in vacuum and at 37°C in vacuum. Results from organoleptic evaluations (Table 15) show very high taste and texture scores for all samples. The values for the samples stored at 37°C seem to indicate a slight increase in preference for that sample after 5 weeks of storage; this could be attributed to a preference for a slightly cooked flavor, developed during storage at an elevated temperature, which was noted among the comments made during the taste evaluation.

Results of an organoleptic evaluation on test samples from the large batch production of 1. freeze-dried whole milk pudding with orange-flavored gel pieces and 2. N.F.D.M. pudding with freeze-dried orange-flavored gel pieces, sent to NASA/JSC, are presented in Table 16.

Table 14

Average Difference Test Scores for Simulated Fruit Gels Incorporated in a Pudding Matrix

Test 1

Sample	Taste	Texture
whole milk/beat	8.20	8.20
N.F.D.M./stir	7.30	6.20
N.F.D.M./beat	7.20	6.00

Test 2

Sample	Taste	Texture
whole milk/w/gel	7.50	6.40
N.F.D.M./w/gel	6.70	5.90

Test 3

Sample	Taste	Texture
whole milk/fresh	8.20	7.50
whole milk/f.d.	7.90	6.60

Table 15

Evaluation of Freeze-dried Whole Milk Pudding with Orange-flavored Gel Pieces After Storage

Taste

Sample	1 Week	2 Weeks	5 Weeks
23°/Air	7.80	7.57	7.88
23°/Vac	8.10	-	8.25
37°/Vac	7.50	8.29	8.25

Texture

Sample	1 Week	2 Weeks	5 Weeks
23°/Air	7.20	7.43	7.75
23°/Vac	7.10	-	7.88
37°/Vac	7.20	7.86	8.00

Table 16

Average Difference Test Scores for Simulated Fruit Gels Incorporated in a Pudding Mix

(Test samples from large batch production after storage for ten days under vacuum at room temperature)

Sample	Taste	Texture
f.d. whole milk/w/gel	7.70	7.30
N.F.D.M./w/f.d. gel	7.80	6.70

4.7 Public Information on AFM

In response to the presentation at the First International Congress on Engineering and Food entitled "Mechanical Properties of Fruit Simulating Alginate Gels," we received a request to submit samples of freeze-dried yoghurt containing the fabricated fruit pieces which have been developed in this contract for exhibition at the Seventh International Food Exhibition (7eme Salon International de l'alimentation) to be held in Paris on November 15-20, 1976. The invitation was transmitted orally by Mr. Gilles Bragadir of APRIA, the sponsoring organization. Freeze-dried fabricated fruit pieces and the final freeze-dried yoghurt product were prepared and sent with an information sheet (copy attached). This information sheet acknolwdges NASA's sponsorhip of this project.

FREEZE-DRIED CALCIUM ALGINATE GELS SIMULATING FRUIT PIECES IN A FREEZE DRIED YOGHURT PRODUCT

PRODUCT: Fruit simulating pieces are fabricated in the two-step gelling process described below. The fabricated gel pieces retain the fruit simulating texture following freezing/thawing or freeze drying and rehydration. The product being displayed is a freeze dried pineapple yoghurt in which the fruit pieces and yoghurt were combined and freeze dried at the same time. It is also possible to dry mix the fruit pieces with freeze dried yoghurt. The fresh, thawed or rehydrated fabricated fruit pieces can be incorporated into dry mixes for gelatin desserts and baked goods, since the gel matrix is stable to heating which occurs in the preparation steps.

PROCESS: The fabricated fruit pieces are composed of calcium alginate, gelatin, pectin, sucrose, and flavoring and coloring. A sodium alginate-containing gelatin gel is prepared by mixing all components and chilling. The gelatin gel is cut into pieces of the desired shape and size, and then placed in a calcium lactate bath for exchange of the sodium ions with calcium, giving the formation of the stable calcium alginate gel. The crosslinked pieces are then subjected to an osmotic concentration against sucrose, removing approximately 1/3 of the gel water. The sample can then be slowly frozen and freeze dried without loss of textural properties.

REFERENCES:

Luh, N., M. Karel and J.M. Flink 1976
A Simulated Fruit Gel Suitable for Freeze Dehydration
J. Fd. Sci. 41: 89 - 93

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5. Osmotic Preconcentration to Yield Improved Quality Freeze-dried Products

5.1 Introduction

Studies on osmotic concentration of fruit were expanded to include concentration of vegetable products prior to freeze-drying (Section 5.4). Organoleptic evaluations and storage stability tests were conducted on some of these products. This work is reported in a technical paper, "Osmotic Concentration of Fruit Slices Prior to Freeze-dehydration," Sections 5.2, 5.3, and 5.4. Section 5.5 includes a discussion of sucrose, lactose, and cheese whey as osmotic agents. This discussion formed a part of an S.M. thesis at M.I.T. by Mr. Rogelio Moreyra Sandoval. Dr. Karel acted as thesis advisor.

5.2 "Osmotic Concentration of Fruit Slices Prior to Freeze-dehydration"

The following paper "Osmotic Concentration of Fruit Slices Prior to Freeze-dehydration" by James Hawkes and James M. Flink was presented at the First International Congress on Engineering and Food (August, 1976). The succeeding section is a preprint of the manuscript for publication in the Proceedings of the First International Congress on Engineering and Food scheduled to appear in the summer of 1978.[1]

[1] Due to unforseen circumstances, I.C.E.F. was not able to meet its projected plans for publication. This manuscript has now been accepted by the Journal of Food Processing and Preservation and is awaiting publication, some time early Spring, 1979.

OSMOTIC CONCENTRATION OF FRUIT SLICES PRIOR TO FREEZE DEHYDRATION

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Contribution Number 3060
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Paper Number 12-09
Presented at the First International Congress
on Engineering and Food,
Boston, Massachusetts
August, 1976

Abstract

Organoleptic quality of freeze-dried foods can be improved by increasing the solids content of the food material to levels of 25 - 35%. This also results in a reduction of the water load to the freeze-drier, which greatly improves the economics of the process. For solid foods, such as fruit slices, the increase in solids concentration is achievable by an osmosis process. Sucrose has generally been the solute of choice, but economic considerations are indicating that the suitability of new osmosis solutes should be evaluated.

Several mixed osmosis solutes were evaluated for their effectiveness in concentrating apple slices prior to freeze-drying. Kinetics of water loss and solute uptake were determined for solutions of differing composition and concentration. Several of the osmotically preconcentrated freeze-dried apple slices were evaluated for organoleptic acceptability.

Introduction

Freeze-drying has long been regarded as a preservation process which yields products of high organoleptic quality. This quality, however, will depend on the process conditions used. For example, it has been shown that the retention of volatile organic compounds (models of flavor components) following freeze-drying of liquid materials depends on the choice of freezing rate and solids concentration of the liquid feed material. Flink (1975a, 1975b) and Thijssen (1975) have reviewed this work. They note that with liquid food systems, retention of flavor compounds was highest with slow freezing and when the initial solids concentration was 25 - 30% or above.

For solid food materials, such as meats, vegetables or fruits, the freezing rate is controllable, but regulation of solids content is difficult. Flink (1975a) reported on the improvement of organoleptic quality of freeze-dried fruit products following an osmotic concentration step, in a 60% sucrose solution, resulting in solids concentrations above 25%.

Ponting, et al (1966a, 1966b, 1973), described a process for removal of 50% of the water of fruit pieces by mixing with dry sucrose, or by immersion in concentrated solutions (65 - 75% solids) of sucrose or invert sugar. They indicate that the final products can be air or vacuum-dried, or dehydrofrozen but do not examine freeze-drying. Farkas and Lazar (1969) conducted further evaluations of the effects of temperature and sucrose concentration on rates of osmotic dehydration. They also report on scale-up

to a pilot plant process. Hope and Vitale (1972) described the application of osmotic dehydration for concentration of banana, plantain and ripe mango using 67% (w/w) sucrose solutions and green mango using 25% (w/w) sodium chloride solution. Pader and Richberg (1968) also describe an osmosis step as a pre-concentration prior to air or vacuum-drying. They note that it is necessary to use a crystallizing sugar, and claim an advantage to sulfite treatment instead of blanching for prevention of browning, since structural integrity of the tissue will be retained. On the same basis, freezing of the tissue is undesirable.

Garcia, et al (1974), found that pretreatment in 65% sucrose, did not affect quality of dried fruit. Dixon, et al (1976), used a combination of osmotic-dehydration and vacuum-drying to produce dry apple slices.

Dymsza (1975) described a process in which solid food products were osmotically dehydrated by immersion in an alkene glycol, such as propylene glycol to produce a shelf-stable product. While there is preservative action associated with the reduction of water content, the infusion of the preservative into the piece is of more significance. Camirand, et al (1968), coated food pieces with a thin calcium pectate membrane. The coated pieces were then immersed in a 75° Brix invert sugar: sucrose solution (50:50) for the osmotic dehydration. The presence of the membrane prevented uptake of the solute by the food piece, but allowed removal of water.

The current study investigates the kinetics of osmotic concentration for solute systems of varying composition and concentration. In particular, several mixed solute systems were considered as a means for reducing the requirement for sucrose.

Materials and Methods

Materials: Reagent grade sucrose and sodium chloride, and commercial lactose (Purity Cheese Co., Mayville, Wisconsin) and maltodextrin of 15 DE (Maltrin-15, Grain Processing Corp., Muscatine, Iowa) were used to prepare osmosis solutions. In addition, sucrose and lactose were evaluated in the dry state for their water removal capabilities.

McIntosh apples were purchased at a local supermarket. At those times of the year when apples were available only from controlled atmosphere storage, care was taken to avoid selecting individual apples with obvious softening of the tissue. Studies were suspended during the summer when apple quality was relatively poor.

Preparation Methods: The osmosis solutions were prepared as pure solute or mixed solute systems with total concentrations generally being 25-60% (w/w). Sodium chloride was examined at concentrations of 5-25% (w/w). All osmosis solutions contained (in addition to the osmotic agents) 0.52% ascorbic acid and 0.14% malic acid to prevent browning of the apple slices during handling and subsequent processing.

Studies on the osmotic preconcentration of fruit slices have been conducted by a variety of methods, including:

1) Agitating fruit in a "static" solution,
2) Static contacting of fruit and solution,
3) Contacting of fruit and solution while the fruit is under vacuum,
4) Mixing of fruit pieces with dry sugar,
5) Flow of solution through a static bed of fruit.

The work reported here will concentrate on the first method, agitating the fruit in a "static" solution. For each experiment, 400 g of osmosis solution of known concentration are placed in a 1 liter graduated cylinder with a motor driven porous plunger which gently agitates the fruit pieces in the osmosis solution by a reciprocating motion. Apples were manually peeled, quartered and the quarters cut into uniform slices of 3-4 mm thickness. Each apple slice was individually weighed and coded by wrapping with a few turns of colored thread. To the 400 g of solution were added 5 slices totaling about 20 grams of wet weight. An excess of osmosis solution was used to limit concentration changes due to uptake of water from the apple slices and loss of solute to the slices. A slice was removed from the osmosis solution at 0, 1/2, 1, 2, 3, and 4 hours for gravimetric determination of the water loss and solids uptake. Refractometric measurements are made on the osmosis solution at these times to monitor changes in concentration.

The water loss and solids uptake can be determined by gravimetric measurement alone if it is assumed that under the conditions used, the solutes present initially in the apple slice will not diffuse against the total solids concentration gradient into the concentrated osmosis solution. The total wet weight (tw) of the apple slice is determined upon removal from the solution and the total solids weight (ws) determined by first freeze-drying followed by drying in a vacuum oven at 50°C for 24 hours. Now, with the assumption given above, and using the coding system which allows knowledge of the initial slice solids (wso) and water (wwo) contents, tne solids gain can be defined as:

$$SG = \frac{(ws - wso)}{(wso + wwo)} \times 100 \quad \text{g solids/100 g initial wet apple} \qquad (1)$$

and the water loss as:

$$WL = \frac{(wwo) - (tw - ws)}{(wso + wwo)} \times 100 \quad \text{g water/100 g initial wet apple} \qquad (2)$$

The total solids at any time is defined as:

$$TS = \frac{ws}{tw} \times 100 \quad \text{g solids/100 g apple} \qquad (3)$$

In a few cases, a different method for conducting the initial fruit-solution contact was investigated. The apple slices with coded threads are put into a 4-liter vacuum chamber, which is evacuated with a mechanical pump to an absolute pressure below 10 torr. While the system remains under vacuum, osmosis solution is allowed to enter the chamber until the apple slices are completely immersed; an excess of solution is used. The system remains under vacuum throughout the length of the experiment, except when samples are removed for analysis. Water loss and solids uptake are measured gravimetrically as described above.

The suitability of dry sugars for osmotic concentration of apple slices was also considered. Fruit slices were mixed with an equal weight of dry lactose, sucrose or lactose/sucrose mixtures. They were agitated periodically by shaking over the 24 hour holding period, the apple slices were rinsed quickly (2-3 seconds) to remove adhering sugar prior to determining water loss and solids uptake. Since kinetics were not being evaluated, color coding was not necessary.

All the osmotic concentration studies were conducted at room temperature (approximately 23°C).

Selected osmosis conditions were chosen for preparation of larger amounts of concentrated apple slices for subsequent freeze-drying. The apples were placed on trays and frozen at -20°C. They were hard frozen in liquid nitrogen prior to insertion in the Virtis freeze-drier (Model 10-MRTR). Drying was conducted at a pressure below 100 mTorr and with the heating plates at

ambient temperature. With the product loading used, the drying time was approximately 48 hours.

Organoleptic evaluations of the dried products were conducted using a nine point hedonic rating difference test with a minimum of 12 trained panelists. Products were tested for quality of taste and texture. The results were analyzed statistically according to Larmond (1970).

Osmosis Kinetics Analysis: Mass transport data of the type given in equations (1 - 3) can be analyzed according to standard techniques used for obtaining diffusion coefficients, assuming unsteady state Fickian diffusion. By means of simplifying assumptions to the infinite series expressions, "diffusion coefficients" can be determined by plotting:

$$C \text{ vs. } (\text{time})^{1/2} \qquad (4)$$

and measuring the slope of the resulting straight lines.

For the unsteady state Fickian diffusion model to exactly apply it is necessary that external solution concentrations remain constant, and that resistance at the surface is negligible compared to internal diffusion resistance. In this analysis, it is assumed that solution conditions remain essentially constant since there is a large volume of osmosis solution relative to the amount of apple slices.

The condition of total mass transfer resistance being internal to the piece is not met in all cases, especially at higher concentrations of osmosis solution. Thus, the transport

coefficients obtained are overall mass transport coefficients or pseudo "diffusion coefficients."

Several different parameters can be used as the concentration term of equation (4). Four choices were considered. Water lost per 100 grams of initial apple sample neglects the effect of solute uptake and does not account for differences of initial water contents of the various apple samples. This presentation presumably is related to water diffusivity, but the changing apple solids content, due to uptake of solute will alter the driving force for water flow beyond that due to the diffusive loss of water alone. Presenting the fraction of initial water which has been lost accounts for differences of initial water contents of the apple samples, but still does not account for changes in solids content due to solute uptake. Using the change in weight percent total solids does not separate the solute uptake from the water loss, but it does measure a parameter of importance in this study, the increase of solids content prior to freeze drying. An improvement is presentation of the percent total solids change on a unit initial total solids basis (i.e., normalized solids content, NSC), so that variations between initial samples can be considered, and this was the method of presentation chosen:

$$(NSC) = K(t)^{1/2} \qquad (5)$$

where K is defined as the mass transfer coefficient.

The mass transport coefficient (K) is determined from the slope of the NSC vs $(t)^{1/2}$ curves. However, it can be recognized

that in practice there is a rapid uptake of solute within the first one-half hour of osmosis which results in a displacement of the effective "initial" solids content for the remainder of the osmosis period. It is possible to define a K value for the overall osmosis process (total solids gained plus water loss) by including all the data points (i.e., including time = 0) in the determination of the slope of the NSC vs. $(t)^{1/2}$ curve. If, however, the zero time data point is omitted, then the "K" value (called K') reflects primarily the water loss, with solids gain subsequent to the rapid initial uptake having a much smaller effect.

The gravimetric data for osmosis of apple slices with 50% sucrose solution (Table 1) is illustrated in Figure 1. The plots of NSC vs. $(t)^{1/2}$ for the 50% sucrose solution are shown in Figure 2. In drawing the regression lines, the zero time point was included in one case and omitted in the other. As noted above, the lines represent the overall K value and the K' value associated primarily with water loss. For the case of the water loss K' value, the higher intercept value reflects the effective NSC value at zero time (i.e., increase in solids due to the rapid uptake of solute).

In this report, K values will be reported since they more closely reflect the interest in change of total solids to a level desired for freeze-drying.

Results and Discussion

Effect of Solute Concentration: The overall mass transport data for osmosis with sucrose are given in Table 1. The normalized solids contents are shown in Figure 3a and 3b as a function of time and $(\text{time})^{1/2}$, respectively. The K values, obtained from the slopes of the lines in Figure 3b, are tabulated (Table 2) with the K' values and their corresponding extrapolated NSC values at zero time (intercept). Also given in Table 2 are the gain of solids content after one-half hour of osmosis (i.e., a measure of the rapid uptake) and the average gain of solids at the end of the osmosis process (average value for 2, 3, and 4 hours). The intercept is a measure of the rapid solids uptake, since in most cases little additional solid is gained after the first hour of immersion (Table 1, Figure 1). K values increase with sucrose concentration; K' values also increase, though 50 and 60% values are about the same. Since most of the solids uptake occurs within the first one-half hour, this would indicate that the rates of water removal are similar for the 50 and 60% sucrose concentrations after this initial solute uptake, which is much greater for the 60% than 50% sucrose concentration. This reflects the increase in intercept value for the K' evaluations.

The K values and average total solids content at the end of the osmosis period for all systems examined are given in Table 3. The effect of concentration on K value and final apple slice solids content is similar to that noted above for the series of sucrose solutions.

Effect of Agitation During Osmosis: In a set of experiments with a different batch of apples (hence slightly different K values), the influence of agitation on the mass transport coefficients was investigated. Figure 4 shows that the gentle agitation used in this study has little effect on osmosis rate and K values at low osmosis solute concentrations. As solution concentration increases, however, and there is a concomitant rise in viscosity and resistance to mass transfer, agitation results in higher K values for agitated systems as compared to the non-agitated system.

Solute Uptake Behavior: During the course of osmosis, the apple slices pick up solute. It has been shown that the solids are gained very early in the process and then increase only very slowly during the remainder of the process (Figure 1, Table 1, 2). While no attempt has been made to measure the spatial distribution of this solute, it is likely to be either located as a thin surface layer, or perhaps in intercellular spaces of the fruit slice.

Table 3 shows the net solute uptake at the latter stages of the osmosis process. It can be seen that for the sucrose solutions, the solute uptake increases as the osmosis solution concentration increases. It was noted that samples prepared with agitation have higher levels of uptake than non-agitated samples and that the uptake values of the mixed solutes for solutions of the same total solids content reflect to some extent the uptake values of the individual components at the concentrations present in the mixed solution.

Effect of Solutes: The mass transport coefficients (K) and the average total solids content (averaged over 3-4 hours) of the apples for the various osmosis solutions are given in Table 3. The dependence of K values and final piece solids content on total solids concentration for a series of osmosis solutions are shown in Figure 5 and 6, respectively.

Lactose has a much lower level of sweetness than sucrose and may also become available in increasing quantities as cheese wheys are recovered and fractionated to recover proteins, leaving a lactose rich fraction. One potential problem is the low solubility of lactose in aqueous solution. The solubility limit for lactose is generally reported to be about 17-20 grams of lactose per 100 grams of solution. In this study, lactose solutions were prepared at concentrations of 25-28% by first heating the solution to dissolve the solids and then allowing the solution to cool to room temperature before use. This undoubtedly resulted in a supersaturated solution, though in all the studies conducted with pure lactose solutions, no nucleation of crystals was observed during the time period of osmotic treatment. Only once in a 25% lactose/35% sucrose mixed system, very small lactose crystals were observed to form after an extended period of standing.

Osmotic preconcentrations of peach slices and banana slices were attempted using lactose solutions at 20 and 28% solids, while a solution at 25% solids was used with apple slices. A pure lactose solution was not promising as an osmosis solute, since only slight preconcentration could be achieved.

Mixed Lactose/Sucrose Solutions: The K values for lactose/sucrose mixtures are given in Table 3. It can be seen (Figure 5) that the K values of the 25% lactose/sucrose mixtures increase with increase in total solids from 40 to 60%.

Lactose solutions near or slightly above their solubility limit in combinations with sucrose at total concentrations of 40, 50 or 60%, give sizeable increases in solids content of the apple slices, which are larger than the sum of the increases which would result from each component at the concentration which is present in the mixture.

Sodium chloride has been tested alone at 5-25% solids and in combination with sucrose at a total concentration of 50% solids. The results show that salt-based solutions are very effective for concentrating apple slices. However, the extent to which NaCl can be used as a substitute for sucrose is probably limited due to its saltiness. Organoleptic tests indicate that even two-step processes (salt, then sugar) will not be successful.

Maltodextrin was evaluated as an osmosis solute, alone at concentrations of 25, 40, and 50% and in combination with sucrose at total solids concentrations of 40% (25% maltodextrin/15% sucrose), 50% (35% maltodextrin/15% sucrose) and 60% (45% maltodextrin/15% sucrose). The measured K values and final apple total solids contents are given in Table 3. It can be seen that maltodextrin can be used as an osmosis solute at higher total solids concentration, or in mixed systems. The 25% maltodextrin is relatively ineffective.

Effect of Total Solids Concentration in Solution: Table 3 and Figure 5 and 6 show the effect of total solids content of the osmosis solution on the mass tranport coefficients (K) and the final total solids in the osmosed apple slices after 4 hours. At the 25% total solids level, salt is as expected by far the best osmosis solute. Sucrose, lactose and maltodextrin solutions at 25% total solids show similar K values and give apple slices of comparable, but low, final solids content.

At 40% total solids in the solution, the final solids content of the apple slices falls within the range 22-28% solids for all solutes tested. Carbohydrate solutions at 50% total solids have similar K values, though sucrose shows a slight disadvantage. These solutions give apple slices with total solids between 29-35% (which is at a desirable level for freeze-drying).

All solutions at 60% solids are effective, having similar K values and giving comparably high levels of total solids in the apple slices. Sucrose again seems to show a slightly higher rate of osmosis, however.

Osmosis with Dry Sugars: Fruit slices were held (with periodic shaking) for 23 hours in dry lactose or sucrose. The results show that while lactose powder is only slightly more effective than saturated lactose solutions in removing water, sucrose is very effective, ending up as a subsaturated solution. With dry lactose a caked region forms, giving a shell of low water permeability around the fruit slice. It appears that this shell prevents further transport of water from the fruit slice.

The osmosis was conducted also with mixed sucrose/lactose systems. The results show (Figure 7) that while there is a decrease in water removal as lactose replaces sucrose (at constant total amount solids), the mixture acts synergistically. The solids content which earlier studies have shown to be desirable for attaining improved freeze-dried quality can be achieved with a dry 50:50 mixture of lactose and sucrose. The presence of the sucrose apparently gives flow paths for water removal from the fruit piece so that all the lactose is available as a moisture sink.

The apple slices preconcentrated with dry sucrose increased from 11 to 36% solids. However, either the loss of water or the rate of total loss was so great with pure dry sucrose that the slices were highly shrunken, giving a poor appearance. This is in contrast to the good appearance which is obtained when the osmotic pre-treatment is achieved using a 60% sucrose solution. Three hours in a 60% sucrose solution gives apple slices of approximately 30% solids. With the mixed dry solids systems, all samples had reasonably good appearance, being only slightly shrunken.

Effect of Vacuum Contacting of Fruit and Solution: Evacuation of the chamber containing the apple slices and contacting with solution while under vacuum gave increased uptake of solids in the initial period of contact as compared to the agitated systems of equal composition (Table 4). It is seen that when osmosis was conducted under vacuum a period of 3 hours was more than adequate to attain the desired total solids

levels, though this was achieved with more solids uptake and less water removal.

Organoleptic Evaluations: Selected, osmotically concentrated freeze-dried apple slices were evaluated in the dry state and following rehydration. Table 5 gives the taste and texture scores on a nine point scale (9 = like extremely; 1 = dislike extremely) for 4 tests on groups of the dried apple slices, and taste scores for rehydrated ground apple, which were generally slightly higher for the mixed osmosis solutes. (Texture of rehydrated samples was not evaluated).

It is seen that high organoleptic scores were attained with the pure sucrose and mixed carbohydrate solute systems. The salt-based systems were unacceptable even when the initial salt osmosis was followed by a sucrose osmosis step. The scores from the first test indicate that the pure sucrose systems were rated somewhat higher than either mixed system. This may reflect a desirable taste effect associated with the sweetness of sucrose. Tests on the effect of total solids content for the mixed carbohydrate solutions indicate that over the range of concentrations considered, the product was uniformly highly acceptable.

Texture for all samples was well rated.

Conclusion

Osmotic dehydration is a successful method of preconcentrating fruit pieces prior to freeze-drying. All osmosis solutions at 60% solids are effective, so that the final choice of the solute system can be made on the basis of organoleptic and economic factors.

Lactose is suitable for use as a partial substitute for sucrose in both dry and aqueous media, although, with its low solubility limit (about 25%), lactose cannot be used alone. In dry systems, a caked layer of lactose forms a barrier around the fruit piece, preventing further transport of water from the sample. Mixing lactose and sucrose alleviates this problem. Organoleptic evaluations have shown high acceptability for apples treated in sucrose-lactose systems. Maltodextrin can also be used as a partial substitute for sucrose. Both maltodextrin and lactose have low levels of sweetness, making them desirable as osmotic agents for food materials requiring less sweetening.

Based on osmosis kinetics, 25% sodium chloride is by far the best osmotic agent. This is undoubtedly due to its higher molar concentration for a 25% weight concentration and its ionization in solution. Even when combined with sucrose, high osmosis rates are observed, but the ability to use sodium chloride is limited in processing fruits due to its saltiness. Organoleptic evaluations of apples processed with sucrose-salt mixtures show them to be acceptable, but salt may be suitable for dehydration of other food materials.

Moderate agitation of the osmosis solution and the apples is desirable, especially at higher solids concentrations. The use of vacuum contacting of solution with fruit pieces gives higher increases of solids content due primarily to uptake of osmosis solute. This occurs since air removed from apple tissue by the evacuation leaves voids that are filled by the solution. It has been observed that the apple sugar content is so elevated that during freeze-drying, there is some collapse of the sample. The dried product is not as crisp (more chewy), as those produced by the agitation system. This may be acceptable to certain food items, though apples are preferred crisp.

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Table 1

Mass Transport Data for Osmotic Concentrations of Apple Slices

Osmosis Solute Concentration	Time (hrs) 0	1/2	1	2	3	4
25% Sucrose						
SG[a]	0	7.6	7.4	7.2	7.7	8.5
WL	0	-7.0	-1.8	-3.5	-0.29	+5.1
TS	12.4	17.4	17.9	17.8	18.6	20.1
NSC	1.00	1.40	1.44	1.44	1.50	1.62
40% Sucrose						
SG	0	10.6	12.6	15.4	12.0	13.2
WL	0	2.9	8.0	16.3	22.1	25.0
TS	12.5	21.4	24.0	28.1	27.4	29.1
NSC	1.00	1.71	1.92	2.25	2.19	2.33
50% Sucrose						
SG	0	12.3	13.5	22.0	17.9	15.9
WL	0	7.7	20.9	17.8	31.0	38.9
TS	11.0	22.2	26.6	31.8	33.1	35.0
NSC	1.00	2.02	2.42	2.89	3.01	3.18
60% Sucrose						
SG	0	18.5	19.7	19.5	22.5	25.5
WL	0	22.0	32.0	27.2	43.3	48.7
TS	10.8	30.4	34.7	32.7	42.2	36.5
NSC	1.00	2.81	3.21	3.03	3.91	3.38

a) SG = Solids Gain (g solid/100 g initial apple)
WL = Water Loss (g water/100 g initial apple)
TS = Total Solids (g solids/100 g apple)
NSC = Normalized Solids Content = $(TS)_t/(TS)_o$

Table 2

Mass Transport Coefficients (K, K') and Solids Gain

for Sucrose Osmosis Solutions

Sucrose Concentration	K[a] ($hr^{-1/2}$)	r[b]	K'[c] ($hr^{-1/2}$)	r	Intercept	Average Solids Gain Initial[d]	Final[e]
25	0.27	0.85	0.15	0.80	1.28	7.6	7.8
40	0.65	0.92	0.46	0.88	1.45	10.6	13.5
50	1.09	0.96	0.88	0.96	1.49	12.3	18.6
60	1.20	0.77	0.87	0.68	2.19	18.5	22.5

a) Mass Transport Coefficient (evaluated with zero time data).

b) Regression Coefficient.

c) Mass Transport Coefficient (evaluated without zero time data).

d) Increase in solids at 1/2 hour.

e) Increase in solids averaged over 2 - 4 hours.

Table 3

Mass Transport Coefficients for Osmotic Preconcentration of Apple Slices Based on Normalized Solids Content

Total Concentration of Osmosis Solution	Mass Transport Coefficient (K) ($hr^{-1/2}$)	Total Solids in Apple Slice[a] (%)
5%		
NaCl	0.11	13.1
10%		
NaCl	0.32	17.7
25%		
Sucrose	0.27	19.4
Lactose	0.19	18.9
Maltodextrin	0.17	15.8
NaCl	0.85	32.3
40%		
Sucrose	0.65	28.3
25% Lactose/15% Sucrose	0.57	29.5
Maltodextrin	0.46	21.5
25%Maltodextrin/15%Sucrose	0.30	22.3
50%		
Sucrose	1.09	34.1
25%Lactose/25%Sucrose	0.81	35.0
Maltodextrin	0.75	29.9
35%Maltodextrin/15%Sucrose	0.67	29.0
15% NaCl/35% Sucrose	1.10	43.5
10% NaCl/40% Sucrose	1.50	49.6
60%		
Sucrose	1.20	39.4
25%Lactose/35%Sucrose	1.05	43.6
45%Maltodextrin/15%Sucrose	1.00	40.3

a) Averaged for 3 and 4 hour periods

Table 4. Mass Transport Data for Vacuum Contacting of Apple Slices and Osmosis Solution

Osmosis Solution	Time of Osmosis (hrs) 0	OV[a]	1/2	1	2	3	4
Vacuum 60% Sucrose							
SG[b]	0	11.9	28.4	24.6	23.9	35.9	--
WL	0	0	8.6	10.9	22.5	35.9	--
TS	9.9	19.6	32.0	30.5	33.5	45.7	
NSC	1.00	1.98	3.23	3.08	3.39	4.62	--
60% Sucrose							
SG	0	--	13.5	17.8	16.5	16.7	22.0
WL	0	--	8.5	20.4	35.4	57.0	42.5
TS	11.8	--	24.1	30.4	34.8	48.0	42.5
NSC	1.00	--	2.04	2.58	2.95	4.08	3.60
Vacuum 35% Sucrose 25% Maltodextrin							
SG	0	19.2	18.4	21.2	19.4	25.1	--
WL	0	-6.4	2.7	10.3	19.6	20.9	--
TS	12.4	25.2	26.5	30.2	31.9	35.8	--
NSC	1.00	2.03	2.14	2.44	2.57	2.89	--
35% Sucrose 25% Maltodextrin							
SG	0	--	12.6	12.0	15.1	14.0	10.9
WL	0	--	16.8	14.8	22.3	31.9	34.3
TS	11.5	--	25.3	24.2	28.6	31.0	29.3
NSC	1.00	--	2.20	2.10	2.49	2.70	2.55

a) OV sample analyzed immediately after contact with osmotic solution.

b) SG = Solids Gain. TS = Total Solids.
WL = Water Loss. NSC = Normalized Solids Content (see text).

Table 5

Organoleptic Scores for Osmotic Preconcentrated

Freeze-dried Apple Slices

Test Number	Osmosis Treatment	Taste Score (DRY)[a]	Sig.[b]	Texture Score (DRY)[a]	Taste Scores (Rehydrated)[a]	Sig.[b]
1	60% Sucrose	7.50	A	7.00	6.45	A
	40% Sucrose	7.58	A	6.75	7.18	A
	15% Sucrose/25% Lactose	6.83	A	6.33	6.64	A
	15% Sucrose/25% Maltodextrin	6.67	A	6.50	6.00	A
2	15% Sucrose/25% Lactose	7.42	A	7.33	7.70	A
	25% Sucrose/25% Lactose	7.17	A	7.17	7.40	A
	35% Sucrose/25% Lactose	7.50	A	7.25	7.90	A
3	15% Sucrose/25% Maltodextrin	6.92	A	6.82	7.17	A
	25% Sucrose/25% Maltodextrin	7.17	A	7.36	7.58	A
	35% Sucrose/25% Maltodextrin	6.58	A	7.36	7.67	A
4	Two Step: NaCl/Sucrose[c]	3.82	A	6.27	-	-
	10% NaCl/40% Sucrose	3.09	B	5.82	-	-
	15% NaCl/35% Sucrose	2.55	B	6.45	-	-

[a] Nine point Hedonic Scale (9=like extremely; 1=dislike extremely).

[b] Significance: Within a test, samples having a different letter are different at a 1% level of significance.

[c] Two step: 1 hour in 25% NaCl, rinsed, 3 hours in 60% sucrose, rinsed.

Figures

Figure 1) Mass transport data for osmotic concentration of apple slices with 50% sucrose solution.

SG = solids gained (g solids/100 g initial wet apple).

WL = water loss (g water/100 g initial wet apple).

TS = total solids (g solids/100 g apple tissue at time of measurement.

Figure 2) Normalized Solids Content for Apple Slices vs $(\text{time})^{1/2}$ when concentrated in a 50% sucrose solution, showing method for determining K and K' values (see text). (K - dashed line; K' - solid line).

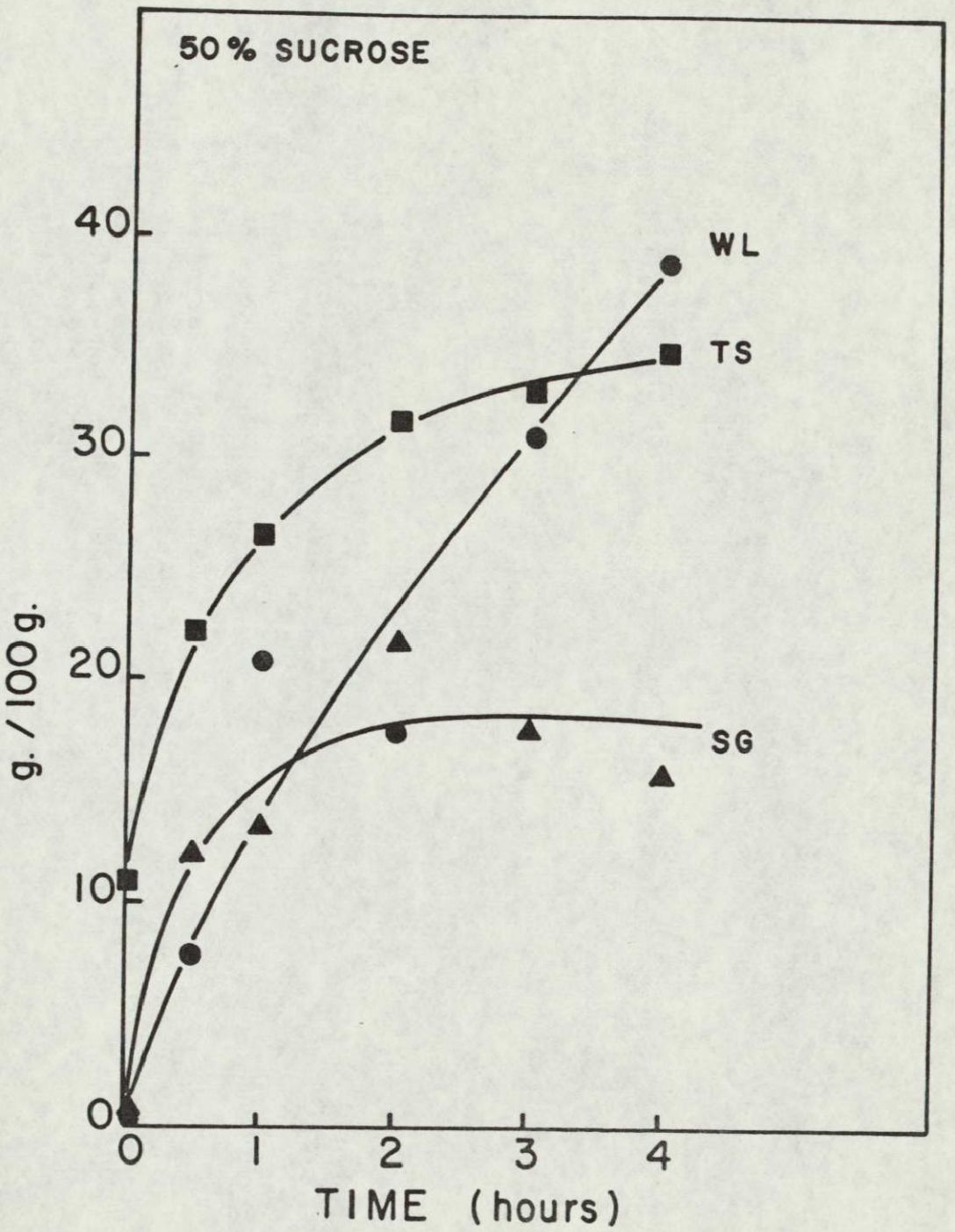
Figure 3) Normalized solids content for osmotic concentration of apple slices in sucrose solutions.

Figure 4) Effect of agitation of apples on mass transport coefficients.

Figure 5) Dependence of mass transport coefficients on solution total solids concentration.

Figure 6) Dependence of final solids contents of apple slices on osmosis solution, total solids concentration.

Figure 7) Mass transport data for osmotic concentration in dry sugar systems (sugar/apples = 1 : 1 by weight).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10
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g. / 100g.
0
1
2
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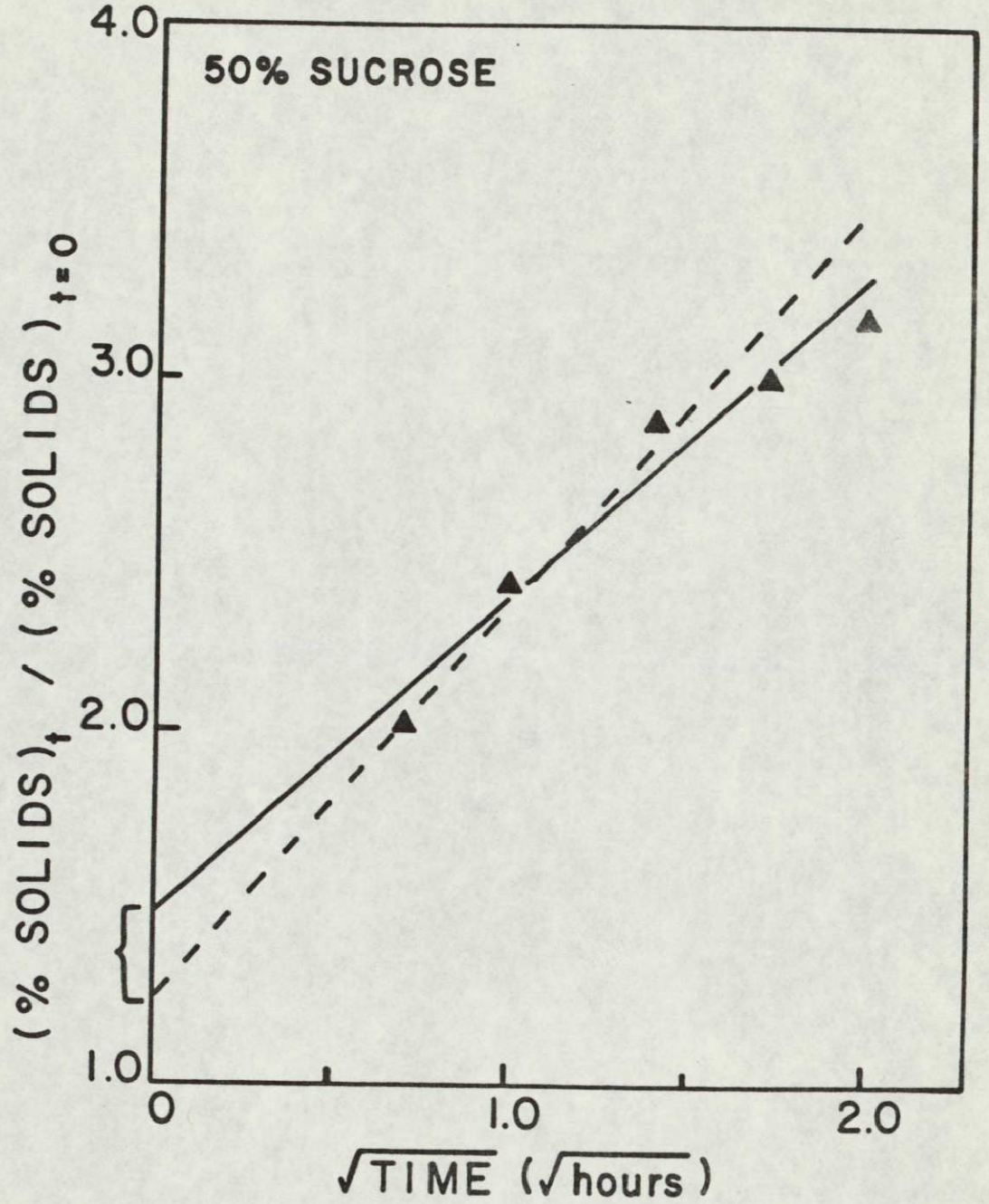
4
TIME (hours)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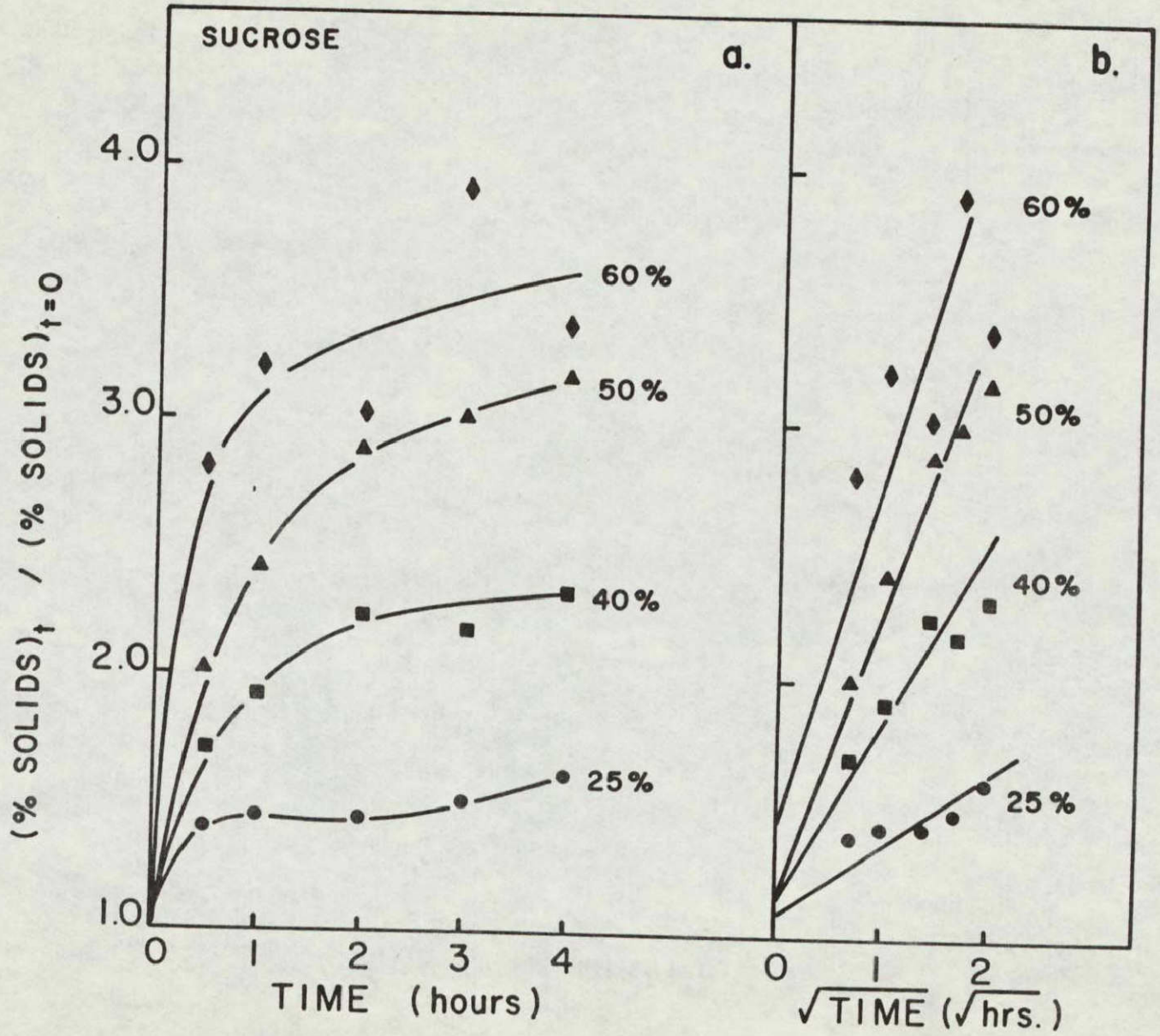
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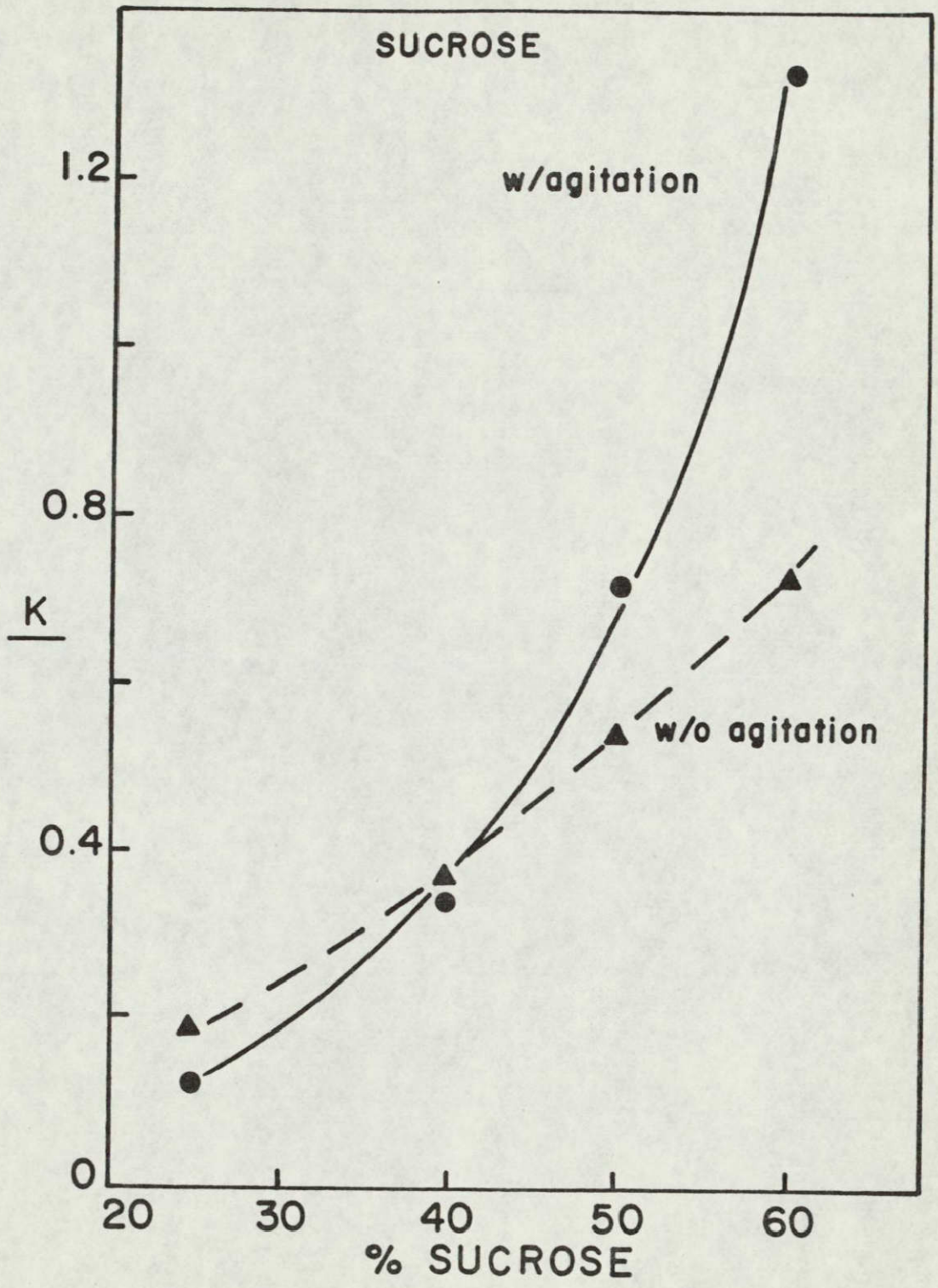
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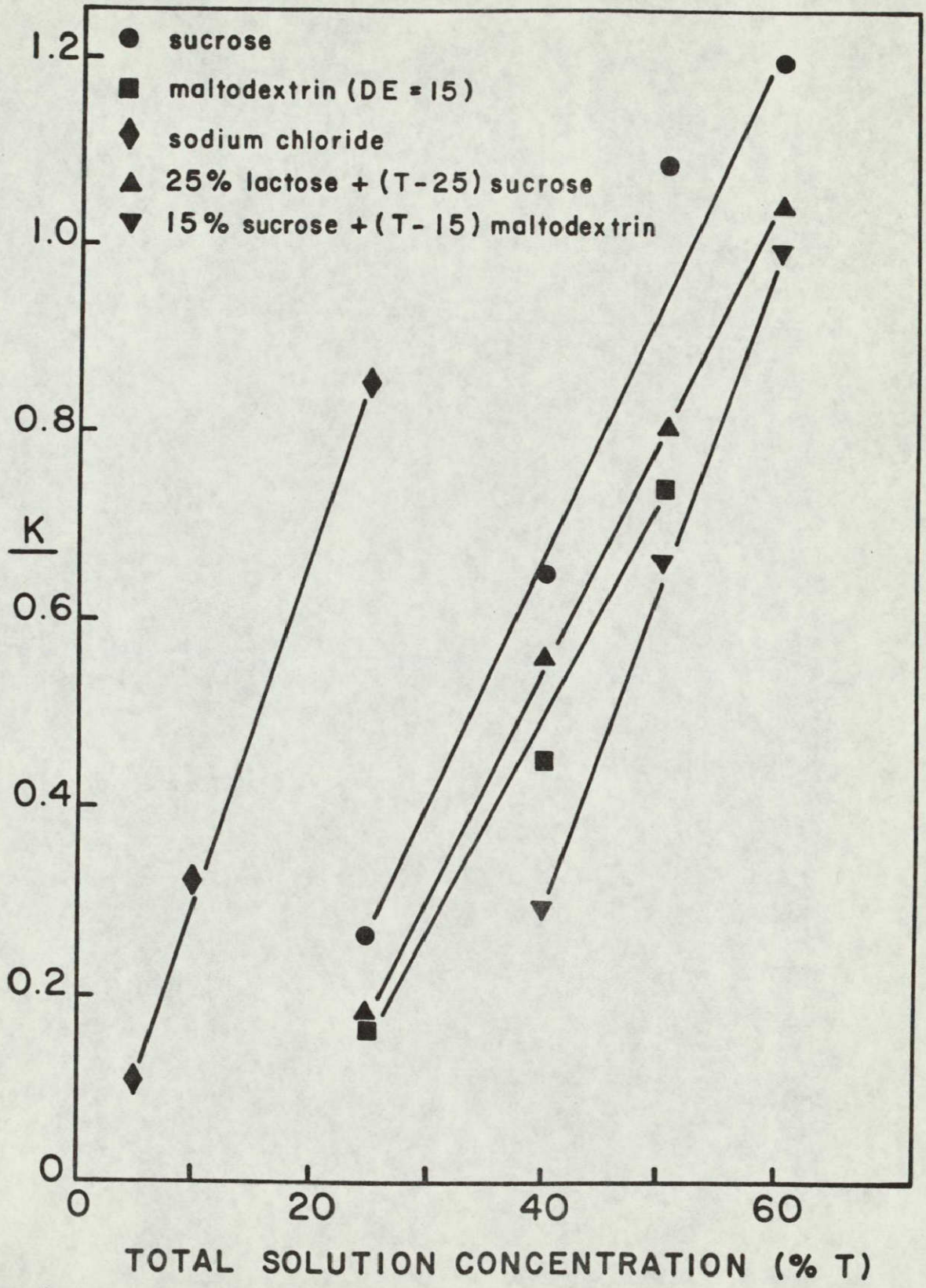
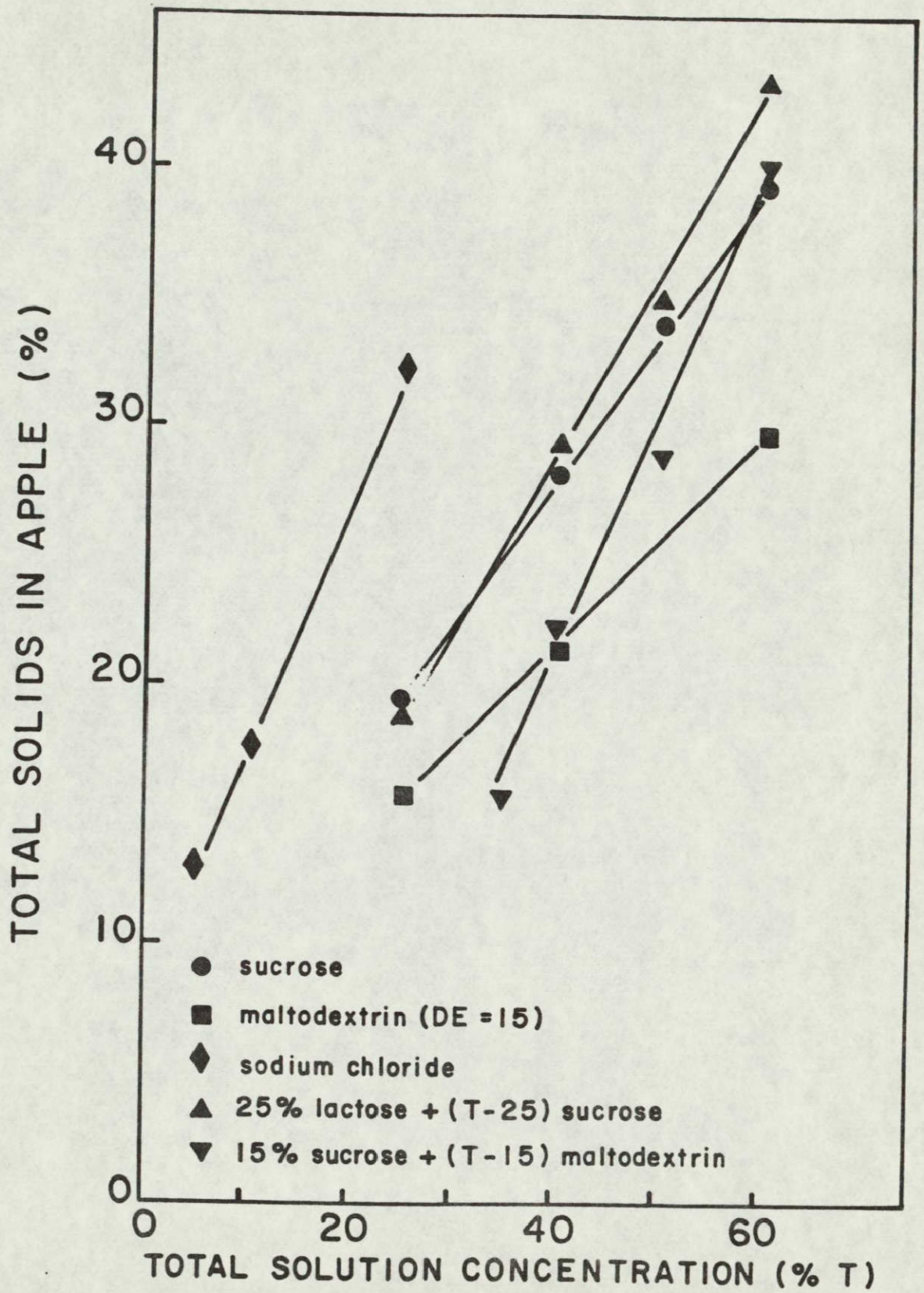
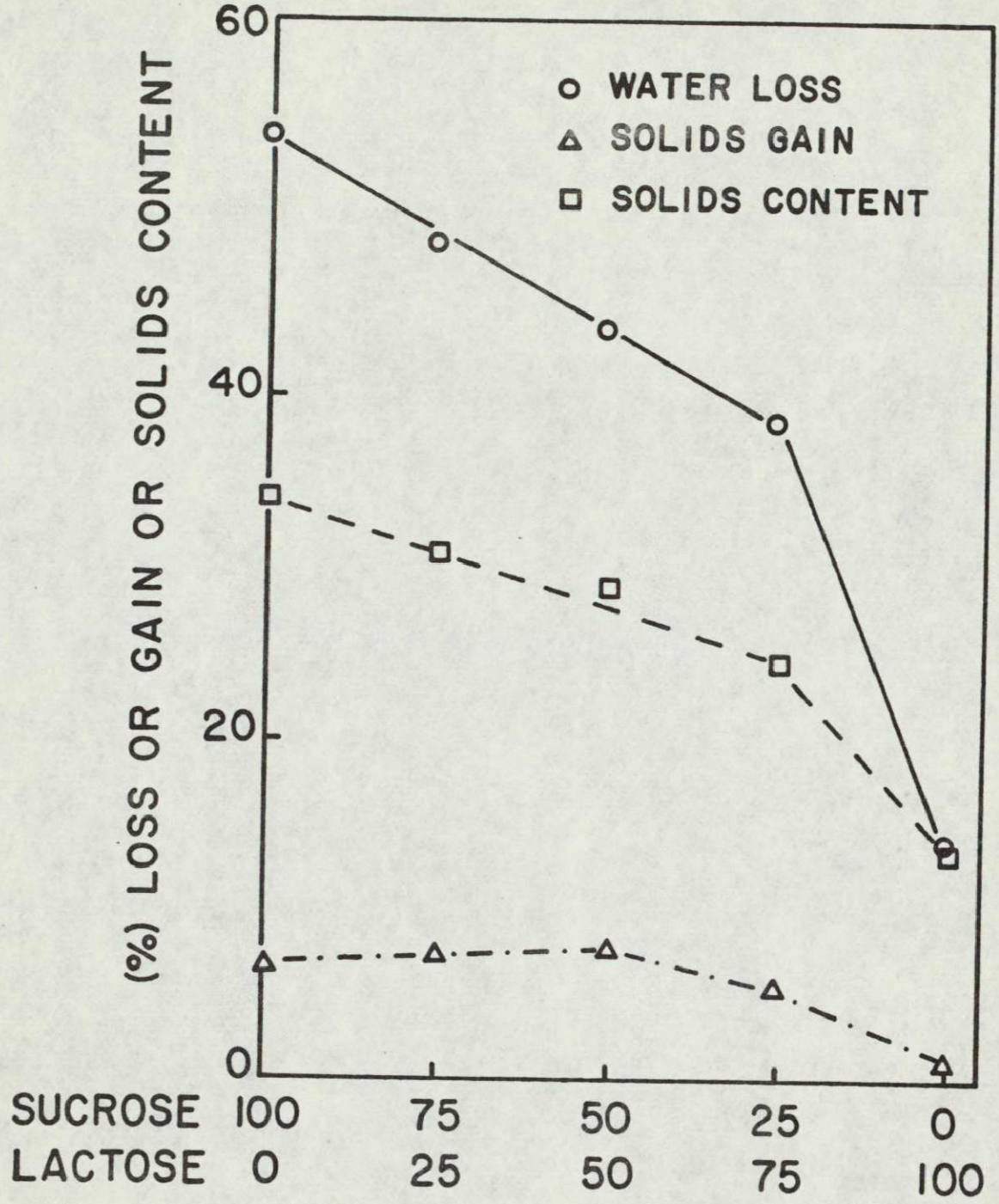

sucrose
maltodextrin (DE = 15)
sodium chloride
25% lactose + (T-25) sucrose
15% sucrose + (T-15) maltodextrin
1.2
1.0
0.8
K
0.6
0.4
0.2
0
0
20
40
60
TOTAL SOLUTION CONCENTRATION (% T)


TOTAL SOLIDS IN APPLE (%)
40
30
20
10
0
0
20
40
60
TOTAL SOLUTION CONCENTRATION (% T)
sucrose
maltodextrin (DE =15)
sodium chloride
25% lactose + (T-25) sucrose
15% sucrose + (T-15) maltodextrin


60
40
20
0
(%) LOSS OR GAIN OR SOLIDS CONTENT
WATER LOSS
SOLIDS GAIN
SOLIDS CONTENT
SUCROSE 100 75 50 25 0
LACTOSE 0 25 50 75 100

5.3 Osmotic Concentration of Fruit Products

Studies on osmotic concentration of fruit products initially reported in the Annual Report-Phase IV have continued to determine the feasibility of using mixed solute systems. More kinetic data was obtained for various osmotic solutes and are presented as MTF values. The rationale for choosing the mass transfer factors (MTF) as the measure of osmosis kinetics and the analytical details for determining the MTF values was given in the Annual Report-Phase IV. Further information on MTF values and the Phase IV studies are given in the paper which is presented as Section 5.2.

A comparison of MTF values for sucrose solutions used during the Phase IV and Phase V studies (Table 1) shows that at the lower concentrations the MTF values of the Phase IV experiments are much lower than for the Phase V experiments. This most likely is because of differences in the tissue structure of the apples because of using samples from different times of the year. The Phase IV studies were mostly conducted during the autumn and winter of 1975 when the apples were newly put into controlled atmosphere (CA) storage. The Phase V experiments date from April and May 1976 when the apples have been in storage for a much longer period and have undergone some changes in structure as is noted by obvious textural changes. At the high sucrose concentration, the large osmotic pressure difference will make the rates

rapid in all cases, and the differences for the apples will be less apparent. Measurements of MTF values on duplicate slices from the same apple gave quite close values.

Organoleptic evaluations which have been conducted on a variety of combinations of products are given in Section 5.2. Aspects not reported in Section 5.2 are evaluations of overall product acceptability and measures of perceived sweetness. Results of evaluations of overall acceptability are given in Table 2, and complete results, not reported earlier, for sucrose-lactose systems are given in Tables 3 and 4 for rehydrated and dry materials.

Organoleptic tests were conducted with apple slices osmotically concentrated in a series of sucrose-lactose mixtures having the following proportions--35 sucrose/25 lactose, 25 sucrose/25 lactose, 15 sucrose/25 lactose. A fourth sample, 60 percent sucrose, was added as a control. Earlier, when a series of sucrose-lactose mixtures was evaluated without the 60 percent sucrose sample, very high scores were obtained in both the dry and rehydrated states (Section 5.2, Table 5). In this later test with the 60 percent sucrose control, some problems associated with browning were noted in the rehydrated systems. However, the samples when evaluated in the dry state were highly rated, though the values were slightly lower than in the previous test. Much lower than normal scores were obtained for the rehydrated taste tests

(Table 3), probably because of the unusual amount of browning that took place in two of the samples, 35% sucrose/25% lactose and 15% sucrose/25% lactose. Included in Table 4 is a ranking test on visual appearance for these rehydrated samples in terms of degree of brown color.

In some cases the degree of sweetness seems to play a part in determining organoleptic acceptability of a product. To evaluate this parameter tests were conducted ranking sweetness in the sample. Tests with sucrose-maltodextrin apples showed that there was a 1 percent significant difference between rehydrated samples with panelists ranking them correctly in order of increasing sucrose concentration (Table 4). (The highest sucrose concentration was ranked the sweetest and also given the highest overall rating in the ranking test; the overall rating however was not significantly different from the other samples.) The tests with sucrose-lactose mixtures also showed that dry samples rated significantly different from each other and were ranked by the panelists in correct order of increasing sucrose concentration. It seems that sweetness may be one factor giving higher scores, though other factors such as reduced acidity could also be of importance.

Towards the end of Phase III a long-term storage stability study was initiated with sucrose pretreated freeze-dried apples; the results of this study were reported in the Annual Report-Phase IV with the exception of one additional organoleptic evaluation which was scheduled for July 1976 just after the

writing of the Phase IV report. To conclude this study, included in this report is a complete table of results including the last data which were collected after 18 months of storage (Tables 5 and 6). Table 5 presents the average test scores for taste and texture of the apples evaluated dry and the average test scores for taste of apples evaluated rehydrated. Table 6 gives the ranking order for the sucrose pretreated freeze-dried apples. The high scores obtained confirm that sucrose treated freeze-dried apples remain acceptable when stored dry over extended periods of time. Similar organoleptic evaluation procedures described in Larmond (Methods for Sensory Evaluation of Foods, Publication 1284, Canadian Dept. of Agriculture), are used throughout this study and all other investigations concerned with sensory testing of products throughout this report. Osmotically concentrated freeze-dried peaches were prepared according to the following method and sent to NASA/JSC in accordance with the provisions of the contract.

1. Fresh whole peaches were peeled, pitted, and sliced; they were immediately immersed in an osmotic solution of 60 percent sucrose, 0.52 percent ascorbic acid, and 0.14 percent malic acid.

2. With gentle circulation of solution, the peach slices were subjected to osmotic drying for approximately 3 1/2 to 4 hours.

3. After osmosis peach slices were drained and rinsed 30 seconds with agitation in a 0.52 percent ascorbic acid solution.

4. Peach slices were spread out on trays, frozen at -25°C, freeze-dried, and vacuum packed.

Two separate batches of about 6 pounds of whole fresh peaches/ 4 liters of solution each were prepared. Storage stability data on freeze-dried peach slices have been previously reported (Annual Report - Phase III, Section 5). These data show highly rated scores for samples treated with sucrose and stored dry under vacuum for 16 weeks. Two organoleptic evaluations of each batch of the osmotic concentrated freeze-dried peaches were conducted; the results showing average difference test scores are reported in Table 7. Both batches have very high test scores.

5.4 Osmotic Concentration of Vegetable Products

Previous studies (Annual Report - Phase IV and Section 5.2. of this report) have indicated that sodium chloride is a particularly effective osmotic agent for water removal from fruit slices. Because of the objectionable salty flavor in fruit, it was decided to evaluate the suitability of salt for osmotic concentration of vegetable pieces prior to freeze-drying.

Vegetable pieces (turnips and carrots) were processed similarly to methods previously described using fruit slices.

Osmosis was conducted using 5-25 percent (w/w) sodium chloride solutions and mixtures of 25 percent lactose with 0-20 percent (w/w) sodium chloride. As expected, increasing solute concentrations of both NaCl and the lactose-NaCl mixtures show increased normalized solids content [$(\%\text{solids})_t$ ($\%$ solids)$_{t=0}$] in the vegetable pieces (Figures 1-4). Samples osmotically treated with high concentrations of lactose-NaCl mixtures have a shriveled appearance. Those with lower concentrations (25% lactose/0-10% NaCl) as well as all the pure salt concentrations have a reasonably good appearance.

Because of the similar osmotic concentration behavior of the turnips and carrots and the higher potential interest in carrots as a freeze-dried product, further studies were limited to carrots. Further studies on osmotic behavior and organoleptic evaluation of freeze-dried carrots used the following basic procedure for sample preparation:

1. Fresh carrots are pared and sliced. For blanched materials carrots are immersed in boiling water for seven minutes.
2. Sliced carrots are osmotically dehydrated in various lactose/sodium chloride solutions for 4 hours. Untreated carrots are immediately frozen and freeze-dried.
3. After 5 hours of dehydration samples are rinsed in a 0.52% ascorbic acid solution for 30 seconds to rinse off adhering surface solute. Samples are then frozen at -25°C and freeze-dried.

4. To rehydrate for organoleptic evaluation, 15 g of dry sample were put in 200 ml of water until rehydrated (30-40 minutes). The solution was then poured off and a fresh 200 ml of water were added. (This removes excess salt leached out from osmotically treated carrots.)
5. Carrots were cooked in boiling water for 30 minutes.

Organoleptic test results from Test No. 1 on carrot slices are presented in Table 8. The following samples were tested: carrots concentrated with 25% lactose/10% NaCl, 25% lactose/5% NaCl, 25% NaCl, and nonconcentrated plain carrots. The two samples which had been concentrated with the mixed lactose/NaCl system were highly rated and essentially equivalent. The normalized solids contents prior to freeze drying for the 25% lactose/15% NaCl and for the 25% lactose/10% NaCl indicates that sizable savings in drying capacity can be achieved for a given product throughout.

Comments on the quality of the nonconcentrated freeze-dried carrot sliced indicated that the omission of a blanching step may have resulted in quality changes (off-flavor formation and color loss) prior to testing. These samples were tested one week after freeze-drying and storing under ambient conditions in air-tight glass jars in darkness. The fact that the osmotically concentrated carrot slices did not show these same changes may indicate that blanching can be eliminated for osmotically concentrated samples. To evaluate this possibility, organoleptic tests were repeated with blanched

samples in Test #2 with the blanching step for nonconcentrated carrots occurring just before freezing for freeze-drying; in the case of the osmotically pretreated samples, blanching occurred immediately before osmosis.

Results confirmed that samples treated osmotically with mixed lactose/NaCl systems were highly rated (Table 9). Since the untreated blanched carrots were also highly rated as opposed to previous results with unblanched carrots (Table 8), it appears that blanching may only be necessary for untreated carrots when storage is only for short intervals (about 1-2 weeks). Longer term storage stability of osmotically preconcentrated freeze-dried carrot slices was conducted over a 6-week period for four kinds of samples: carrot slices osmotically treated for four hours with a 25% lactose/10% NaCl mixture (with and without prior blanching) and plain sliced carrots (also with and without blanching). All samples were frozen after preparation, freeze-dried, and stored dry in air in sealed containers kept in darkness (Test No. 3).

After freeze-drying both osmotically treated samples appeared slightly shriveled, whereas both plain samples retained good shape. Upon rehydration, however, the osmotically treated samples regained their original round shape and no visual difference from the plain samples was detected. No change in appearance took place after one week of dry storage. All but the plain unblanched carrot slices were rated well (Table 10).

Both osmotically treated samples retained the same appearance with good orange color after six weeks of storage. The plain carrot samples, however, lost most of their original color to become pale yellow-white; this was slightly more noticeable with the unblanched plain carrot slices. Only the unblanched osmotically treated carrot slices were rated highly with respect to taste. The major adverse comment was the presence of an oxidative flavor. All samples were rated well with respect to texture.

A similar test to study the influence of vacuum on product quality during storage was conducted. Results are reported in Table 11. The results seem to indicate that a vacuum has an effect on the storage of plain, blanched, and unblanched carrots. For osmotically preconcentrated carrots, the differences between storage in a vacuum or in air are small. In the presence of a vacuum there is less deterioration of plain nonconcentrated carrots; the orange color is that of fresh carrots even after 18 weeks of storage. The plain nonconcentrated samples stored in air, however, lost their color after only two weeks of storage. All samples stored under vacuum seemed to develop an oxidized flavor, although less noticeably with the osmotically preconcentrated blanched carrots.

The overall rating of the carrots was affected by personal preferences with respect to saltiness. Even after soaking the freeze-dried osmotically treated carrots for 45 minutes and changing the water before cooking, there was a definitely

perceivable salty flavor.

Osmotic concentration of carrot slices with lactose/NaCl mixtures allows an increase in storage life of freeze-dried carrots. Although a specific study was not conducted, it was observed that the cooking time may be greatly reduced. The major drawback with these carrots when served alone is the salty flavor. The process of osmotic concentration with lactose/NaCl mixtures could be applied to carrots in combination with other vegetables as well as with additional seasonings, flavors, etc. These products would then contain all the necessary salt and seasonings to be added to such preparations as soups, casseroles, etc.

Table 1

Mass Transport Factors for Osmotic Preconcentration of Apple Slices Using Sucorse Solutions

Sucrose Concentration (%)	MTF $(hr)^{-1/2}$	
	Phase IV	Phase V
25	0.12	0.27
40	0.34	0.65
50	0.72	1.09
60	1.33	1.20

Table 2

Results of Ranking Test on Apples

A. Evaluation of Sucrose-Maltodextrin Mixtures

Dry						Rehydrated					
	General						General				
Treatment	Significance of Difference			Score		Treatment	Significane of Difference			Score	
	A	B	C				A	B	C		
35 suc./25 mal.	A	0	0	0	.213	25 suc./25 mal.	A	0	0	0	.142
25 suc./25 mal.	B	0	0	0	0	35 suc./25 mal.	B	0	0	0	.071
15 suc./25 mal.	C	0	0	0	-.213	15 suc./25 mal.	C	0	0	0	-.213

B. Evaluation of Sucrose-Lactose Mixtures

Dry						Rehydrated					
	General						General				
Treatment	Significance of Difference			Score		Treatment	Significance of Difference			Score	
	A	B	C				A	B	C		
35 suc./25 lac.	A	0	0	0	.071	35 suc./25 lac.	A	0	0	0	.340
25 suc./25 lac.	B	0	0	0	-.0355	15 suc./25 lac.	B	0	0	0	-.085
15 suc./25 lac.	C	0	0	0	-.0355	25 suc./25 lac.	C	0	0	0	-.255

C. Evaluation of Sucrose-Sodium Chloride Mixtures

Dry (only)						
	General					
Treatment	Significance of Difference				Score	
	A	B	C	D		
60 suc.	A	0	1	1	1	1.03
*2-step	B	1	0	5	1	.039
10 NaCl/40 suc.	C	1	5	0	5	-.333
15 NaCl/35 suc.	D	1	1	5	0	-.737

Table 3

Results of Taste Tests on Apples-Evaluation of Sucrose-Lactose Mixtures

A. Difference Test

Dry

Taste				Texture			Rehydrated Taste		
Treatment	Significance of Difference	Score	Treatment	Significance of Difference	Score	Treatment	Significance of Difference	Score
	A B C D			A B C D			A B C D	
60 suc.	A 0 0 1 1	7.18	25 suc./25 lac.	A 0 0 0 0	6.09	60 suc.	A 0 0 1 1	7.15
25 suc./25 lac.	B 0 0 0 0	6.64	35 suc./25 lac.	B 0 0 0 0	6.00	25 suc./25 lac.	B 0 0 1 1	6.69
35 suc./25 lac.	C 1 0 0 0	6.27	60 suc.	C 0 0 0 0	5.82	35 suc./25 lac.	C 1 1 0 0	5.00
15 suc./25 lac.	D 1 0 0 0	6.27	15 suc./25 lac.	D 0 0 0 0	5.73	15 suc./25 lac.	D 1 1 0 0	4.69

B. Ranking Test

Dry

General			Rehydrated General		
Treatment	Significance of Difference	Score	Treatment	Significance of Difference	Score
	A B C D			A B D C	
60 suc.	A 0 0 0 0	.281	60 suc.	A 0 0 1 1	.703
25 suc./25 lac.	B 0 0 0 0	.060	25 suc./25 lac.	B 0 0 1 1	.264
35 suc./25 lac.	C 0 0 0 0	.055	35 suc./25 lac.	C 1 1 0 0	-.432
15 suc./25 lac.	D 0 0 0 0	-.396	15 suc./25 lac.	D 1 1 0 0	-.535

Note: In Tables the level of significance between treatments is indicated as follows: 0=no significant difference; 1=significant difference at the 1% level; 5=significant difference at the 5% level.

Table 4

Results of Ranking Tests on Apples

A. Evaluation of Sucrose-Lactose Mixtures

Dry

Sweetness*

Treatment	Significance of Difference				Score
	A	B	C	D	
60 suc.	A 0	0	1	1	.715
35 suc./25 lac.	B 0	0	0	1	.217
25 suc./25 lac.	C 1	0	0	0	-.253
15 suc./25 lac.	D 1	1	0	0	-.678

Rehydrated

Sweetness*

Treatment	Significance of Difference				Score
	A	B	C	D	
60 suc.	A 0	1	1	1	.848
25 suc./25 lac.	B 1	0	5	1	.100
35 suc./25 lac.	C 1	5	0	0	-.393
15 suc./25 lac.	D 1	1	0	0	-.554

Color**

Treatment	Significance of Difference				Score
	A	B	C	D	
35 suc./25 lac.	A 0	1	1	1	.969
15 suc./25 lac.	B 1	0	1	1	.361
25 suc./25 lac.	C 1	1	0	0	-.604
60 suc.	D 1	1	0	0	-.726

B. Evaluation of Sucrose-Maltodextrin Mixtures

Rehydrated (only)

Sweetness*

Treatment	Significance of Difference			Score
	A	B	C	
35 suc./25 mal.	A 0	1	1	.815
25 suc./25 mal.	B 1	0	1	-.035
15 suc./25 mal.	C 1	1	0	-.779

*Rank #1 indicates highest level of sweetness.

**Rank #1 indicates highest degree of brown color.

Table 5

Hedonic Test Scores for Organoleptic Difference Test for Stored Sucrose Preconcentrated Freeze-dried Apple Slices

Time	22/0/V[a]	4/0	22/0	37/0	22/10	37/10	22/43	37/43
			TEXTURE (DRY)					
0 wk			6.75		6.75		3.67	
2 wk		7.31	7.15		7.15	7.23	3.85	3.62
5 wk	7.08	6.42	7.08	6.83	7.25	6.42	4.67	4.75
8 wk	6.75	7.08	7.00	6.08	6.42		4.58	
16 wk	6.82		7.27	6.64				
6 mo	7.40		7.67					
8 mo	7.80	7.70	7.40					
12 mo	7.00		7.00					
18 mo	7.17	6.75	6.67					
			TASTE (DRY)					
0 wk			7.33		7.25		6.92	
2 wk		7.85	7.31		7.38	7.08	5.92	4.62
5 wk	7.25	6.75	7.33	6.50	7.33	6.17	6.42	5.67
8 wk	6.83	7.58	7.08	5.42	6.17		5.42	
16 wk	7.18		7.64	6.91				
6 mo	7.47		7.67					
8 mo	7.70	8.10	7.40					
12 mo	7.42		7.17					
18 mo	7.42	7.42	7.75					
			TASTE (REHYDRATED)					
0 wk			7.60		7.70		7.40	
2 wk		7.42	7.33		7.00	7.42	5.75	5.83
5 wk	7.40	8.00	7.70	7.30	7.10	6.60	7.00	5.20
8 wk	7.67	7.17	7.75	6.33	6.92		5.08	
16 wk	7.00		7.58	6.50				
6 mo	[b]8.31		7.92					
8 mo	[c]7.45	7.72	7.36					
12 mo	7.75		7.67					
18 mo	7.08	6.77	7.46					

[a]Storage conditions: Temperature (°C)/Relative Humidity (%)
V = Vacuum sealed; all other samples sealed in air

[b]Commercial applesauce = 7.62

[c]Commercial applesauce = 6.18

Table 6

Ranking Order for Stored Sucrose Preconcentrated Freeze-dried Apple Slices

Time	1st.	2nd.	3rd.	4th.	5th.	6th.	7th.	8th.
			Evaluated Dry					
0 wk	22/0[a]	22/10	22/43					
2 wk	4/0	22/10	37/10	22/0	22/43	37/43		
5 wk	22/0	4/0	22/10	22/vac[b]	37/10	22/43	37/0	37/43
8 wk	4/0	22/0	22/vac	22/10	37/0	22/43		
16 wk	22/0	22/vac	37/0					
6 mo	22/0	22/vac						
8 mo	4/0	22/0	22/vac					
12 mo	22/vac	22/0						
18 mo	22/0	22/vac	4/0					
			Evaluated Rehydrated					
0 wk	22/0	22/10	22/43					
2 wk	22/0	4/0	37/10	22/10	37/43	22/43		
5 wk	4/0	22/0	22/vac	37/0	22/10	22/43	37/10	37/43
8 wk	22/0	4/0	22/vac	22/10	37/0	22/43		
16 wk	22/0	22/vac	37/0					
6 mo	22/vac	22/0	"C"[c]					
8 mo	4/0	22/0	22/vac	"C"				
12 mo	22/vac	22/0						
18 mo	22/0	4/0	22/vac	"C"				

a: Sample code - Temperature (°C)/Relative humidity (%)

b: 22/vac - at 0% R.H. in vacuum sealed cans

c: "C" is commercial applesauce

Table 7

Average Difference Test Scores
for Freeze-dried Peaches

	No. Panelists	Taste	Texture
Batch 1	13	7.85	7.31
Batch 2	8	8.38	8.25

Figure 1. Time of osmotic treatment of turnip slices with different NaCl concentrations versus normalized solids content ($[\%\ solids]_t/[\%\ solids]_{t=0}$).

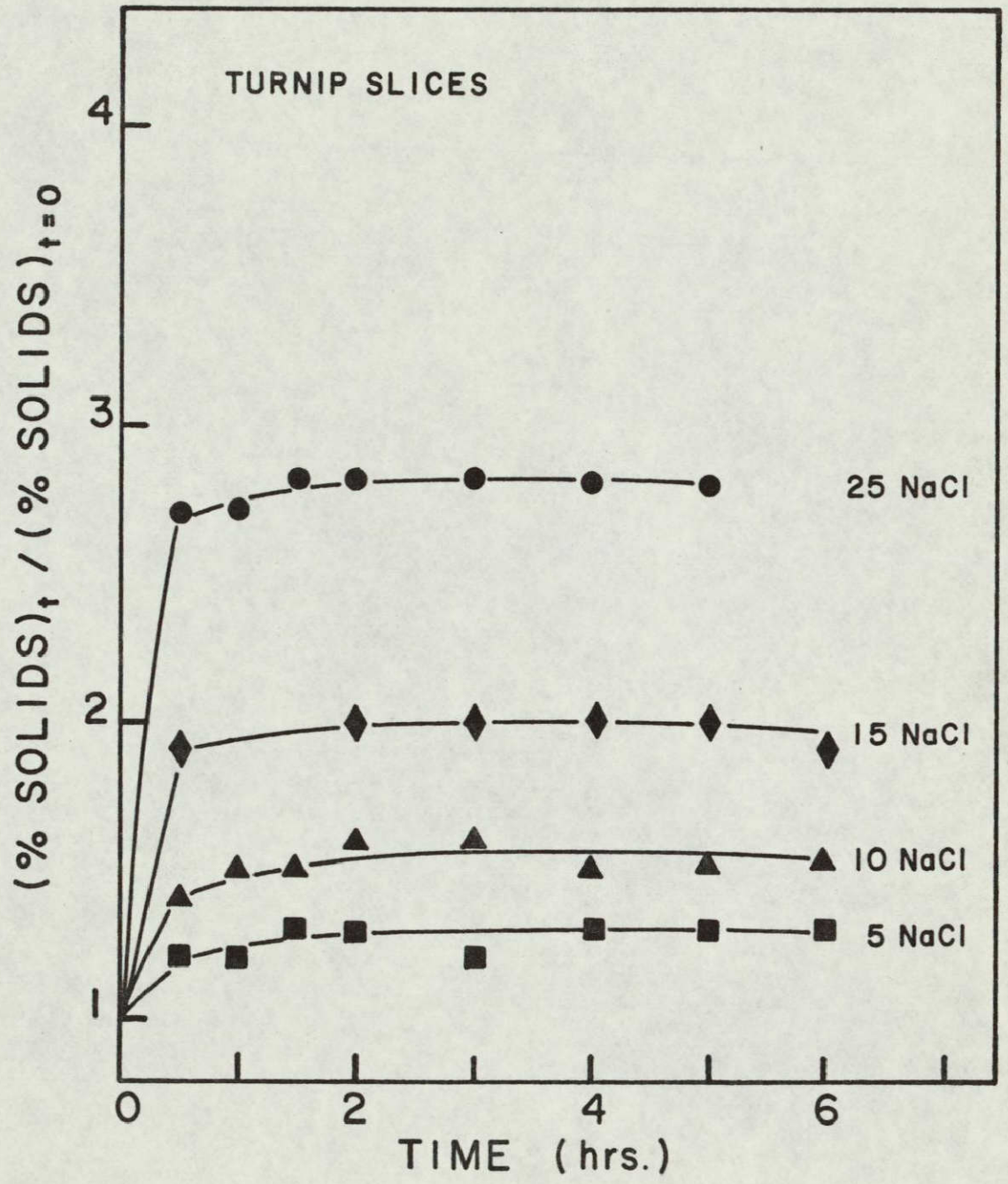


Figure 2. Time of osmotic treatment of turnip slices with different lactose/NaCl concentrations versus normalized solids content.

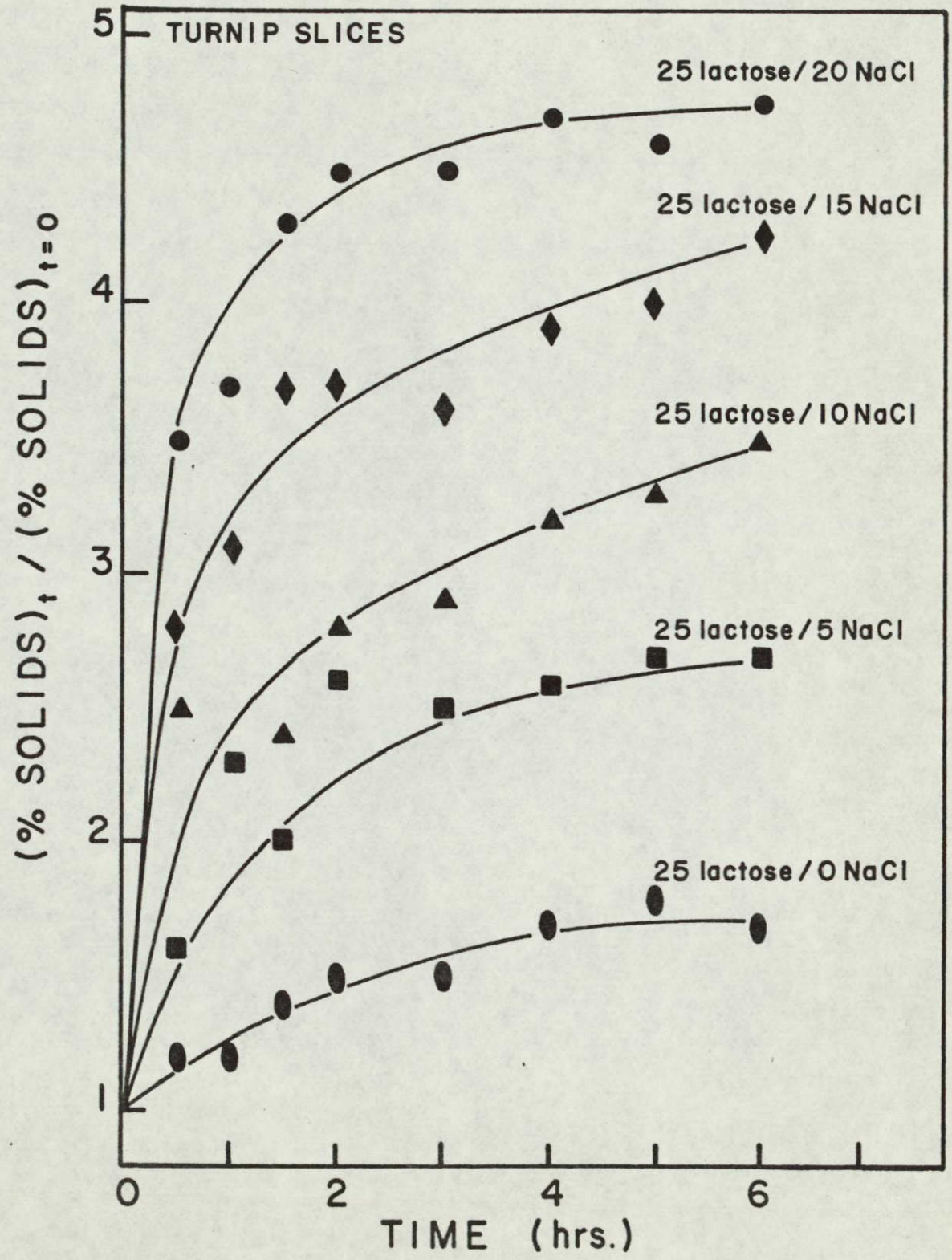


Figure 3. Time of osmotic treatment of carrot slices with different NaCl concentrations versus normalized solids content.

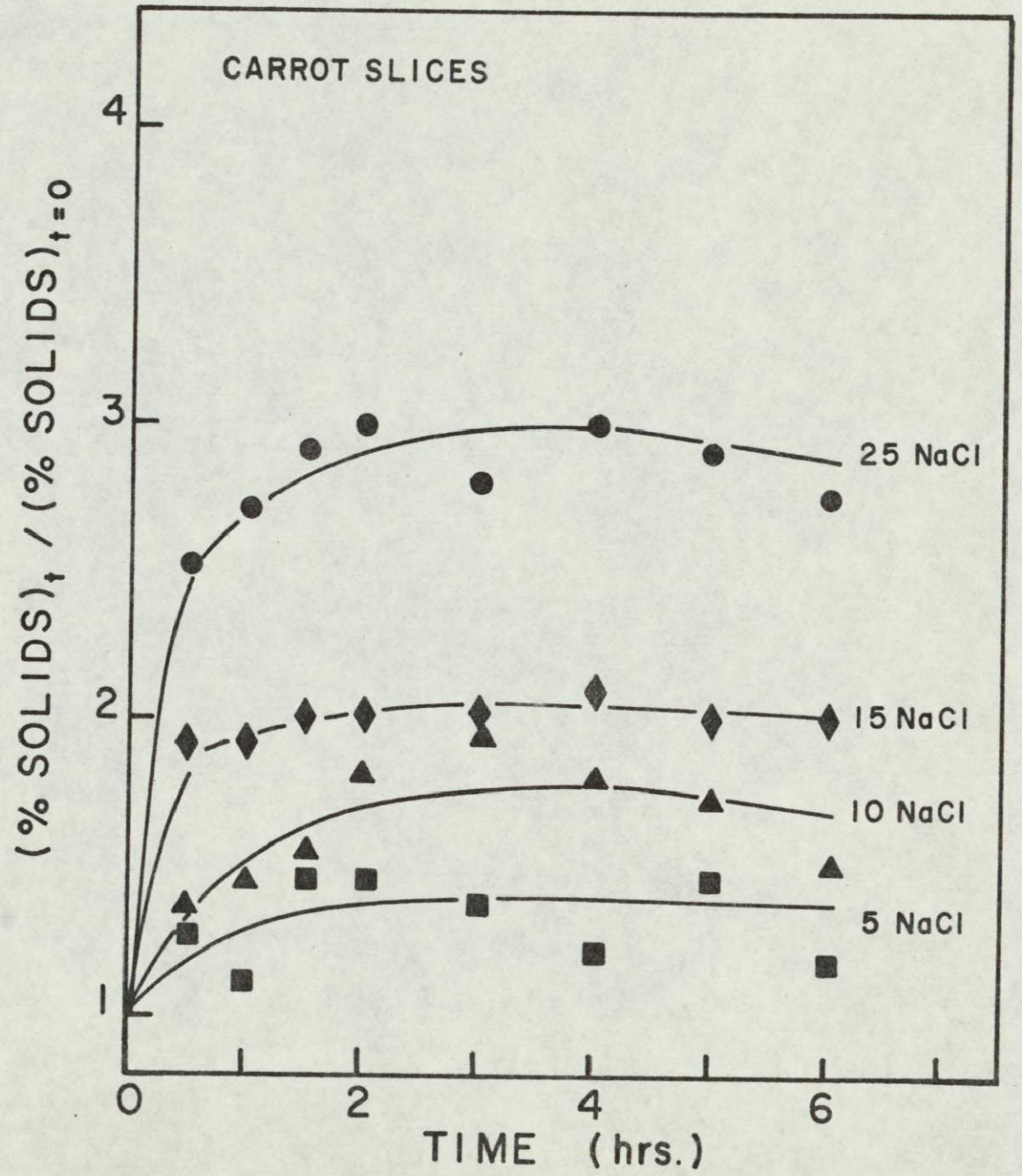


Figure 4. Time of osmotic treatment of carrot slices with different lactose/NaCl concentrations versus normalized solids content.

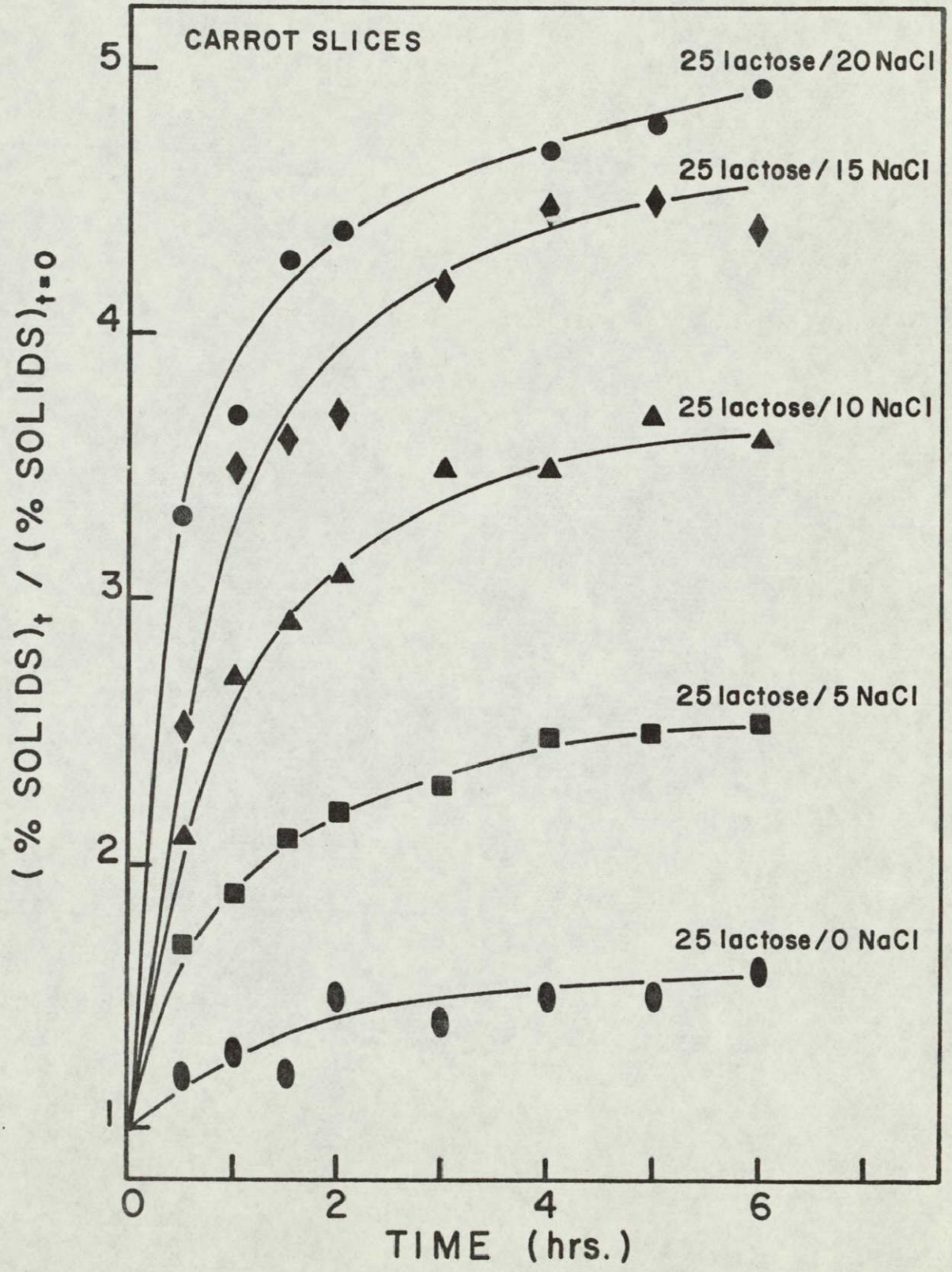


Table 8

Test No. 1

Results of Organoleptic Test for Carrot Slices
Freeze Dried Following Osmotic Treatment
Without Blanching

	Taste[a]	Texture[a]	Ranking	Normalized[b] Solids Content
25% lactose/10% NaCl	6.47	6.09	0.618	2.7
25% lactose/5% NaCl	6.36	6.73	0.519	2.0
25% NaCl	5.00	4.55	-0.399	2.4
No Osmosis	4.45	5.27	-0.738	1.0

a) 9 point scale
b) % solid at end of ɔmosis/% solids initial

Table 9

Test No. 2

RESULTS OF ORGANOLEPTIC TESTS ON CARROT SLICES FREEZE-DRIED FOLLOWING OSMOTIC TREATMENTS (WITH BLANCHING)

Osmotic Treatment	Rating[a] Taste	Texture	Ranking	NSC[b]
25% lactose/5% NaCl	7.15	6.75	.442	2.2
25% lactose/10% NaCl	6.00	6.00	.294	2.6
no osmosis	6.08	6.33	.135	1.0
25% NaCl	2.46	5.08	-.872	2.2

a. Nine point scale

b. Percent solids after osmosis/percent initial solids after blanching

Table 10

Test No. 3

Difference Test Scores of Stored Freeze-dried Carrots

(In Air)

A. Taste

Sample	1 week	6 weeks
Unblanched-25 lactose/10 NaCl	6.53	7.20[b]
Blanched-25 lactose/10 NaCl	6.15	4.50
Unblanched plain	4.46[a]	3.60
Blanched plain	6.15	3.10

B. Texture

Sample	1 week	6 weeks
Unblanched-25 lactose/10 NaCl	6.08	6.80
Blanched-25 lactose/10 NaCl	6.00	6.40
Unblanched plain	5.08	5.40
Blanched plain	6.25	6.10

a. 1% significant difference from all other samples

b. 1% significant difference from all other samples

Table 11

Test No. 4

Difference Test Scores of Stored Freeze-dried Carrots

(In Vacuum)

A. Taste

Sample	2 weeks	9 weeks	18 weeks
Unblanched-25 lactose/10 NaCl	6.50		5.10
Blanched-25 lactose/10 NaCl	5.30	5.75	5.80
Unblanched plain	5.50	6.63	5.30
Blanched plain	5.30	5.13	5.40

B. Texture

Sample	2 weeks	9 weeks	18 weeks
Unblanched-25 lactose/10 NaCl	5.83		4.70
Blanched-25 lactose/10 NaCl	5.50	7.00	5.20
Unblanched plain	6.67	6.25	6.10
Blanched plain	6.00	6.38	6.80

5.5 "Sucrose, Lactose, and Cheese Whey as Osmotic Agents in the Osmotic Dehydration Process of Apples" by Rogelio Moreyra Sandoval. Excerpts from master's thesis.

1. INTRODUCTION

The osmotic dehydration operation consists in the partial removal of water from a material immersed into a concentrated solution, by virtue of a water activity gradient between the material and the solution. It is obvious that the lower the water activity of the solution the larger the gradient and therefore the higher the water removal rate results.

The operation has been used so far as an intermediate step in the complete dehydration process of the materials, these being mainly fruits and vegetables. After the osmotic operation, air, vacuum or freeze drying have been tested,giving each one of these methods different results in terms of quality of the final product and economics of the overall process.

Apples, bananas, mangos, appricoats and many other products have been held to the osmotic dehydration operation, succesfully in many instances.

Apples have been an often studied product as it has proved that they possess a number of advantages over other fruits, such as high porosity which allows water to be removed relatively easy and firm texture which preserves shape and dimensions close to the original.

In this research the drying method after the osmotic operation was freeze drying, and the two main reasons to use the osmotic operation step were: 1.) To optimize the retention of flavor compounds, which ocurrs when the solids content of the material to be freeze dried is 25-30 % or above, (Flink, J., 1975a, Flink, J., 1975b, Thijssen H. A. C. 1975) and 2.) To improve the economics of the whole process, as the load of water to the freeze drier is reducod.

Osmotic dehydration is still improperly understood and research is required to improve it in several aspects, for instance:

a) To understand what are the basic regulatory mass transport mechanisms by which it takes place as a function of all the process variables.

b) To find newer and more efficient osmotic agents which give more flexibility to the process or to the product characteristics. For example, sucrose has been thus far the main osmotic agent used both at industrial and laboratory level. There is information about the risks that the excess of it in the daily diet present (Jalliffe, N., 1975, Sherp, H. W., 1971). On the other hand, the price of sucrose is rather high.

c) Optimization of the process at industrial level, depending upon what kind of finishing dehydration method is applied. This optimization can be related with both the process variables and the equipment.

The specific objectives of this research were:

1.) To determine the mechanisms of transport of water leaving the sample and solute penetrating it, as well as to obtain a quantitative estimation of the limiting transport parameters.

2.) To find out the influence of process temperatures and method of contacting between samples and osmotic solution for a number of osmotic agents tested individually or in combination, on the rate of water removal from and net solids uptake by the sample, as well as on the organoleptic quality of the apple samples after they have been subjected to the whole process, that is, partial remotion of water by osmosis, freeze drying and rehydration.

4. RESULTS AND DISCUSSION

4.1. Mechanism of mass transfer during the osmotic dehydration process of apples.

Before looking into the effects of several process parameters on the rate of water removal, solids content change and organoleptic and microbiological characteristics of the final products, we will adress ourselves to the task of understanding the mechanisms of mass transfer during the osmotic dehydration of apple pieces. In order to do this we will use the results of the experiments performed according to the process described in section 3.1.

4.1.1. Water removal

Table 2 shows the weight percentage moisture content of each one of the rings cut off the cylindrical cross-sections of the apple as a function of temperature, time and mean distance of each section from the surface of the original cylinder.

A graphical moisture distribution for two examples is shown in figures 6 and 7. An immediately recognizable effect is that the higher the osmotic solution temperature, the lower the final moisture content of each one of the different sample regions. This effect is expected (Farkas, 1969). The external sections of the sample which are in direct contact with the solution undergo more dehydration than those in the inner regions. This is also expected since the transfer paths are shorter and water activity gradient is more rapidly established.

One of the possibilities for the controlling mechanism of water migrating out of the sample is diffusion, in which case the phenomenon would be described by Fick's second law.

In order to find out if the experimental data fit the mathematical

model given by the second Fick's law, the average moisture content of single cross sections was used to calculate the average diffusion coefficient. The value for those diffusion coefficients are presented in table 3.

The diffusion coefficients increased with increasing temperature. There was only a small variation within the three different sampling times at a given temperature. Higher diffusion coefficients were obtained for longer process time. This is very likely due to a combination of two factors: 1.) The sample tends to shrink and the total effective diffusional path way becomes shorter, and 2.) Solids uptake decreases the relative moisture content expressed as g H_2O / g sample. The calculation procedure described in section 3.4.1. uses the unremoved water fraction E to calculate D. Since the solids uptake increases with time, the apparent E value will be lower than the one obtained if solids uptake would not take place. A lower value of E gives a higher value of the group Dt/a^2 and therefore a higher D value.

The temperature dependence of diffusion coefficients closely follows the Arrhenius equation

$$D = D_o \exp (- E_a / RT)$$

Where D = diffusion coefficient

D_o = constant

E_a = energy of activation

R = gas constant

T = temperature

A plot of log D versus 1/T (Figure 8) gives a straight line determined by the least square fitting method with slope = -2667 and correlation coefficient = 0.995. The corresponding energy of activation is 12 Kcal/mole.

Table 4 presents the values for the calculation of the theoretical

water concentrations for a given mean distance from the surface of the sample, and also shows the experimental ones and the difference for each case. In order to have a statistical estimation of how close were theoretical and experimental concentrations, the mean and the standard deviation for those differences were computed. The standard deviation was 3.69 for a mean m = 5.98 g H_2O/ g sample.

Figure 6 and 7 show graphically how the experimental concentrations approximate the theoretical ones.

4.1.2. Sucrose uptake

The sucrose content of each sample is presented in table 5 as a function of time and temperature. Similarly to the situation of water removal, the higher the process temperature the higher the concentration of sucrose. Furthermore, the higher the temperature, the more evenly is the sucrose distributed throughout the cylinder sections. Diffusion coefficients for sucrose were calculated in the same way as for water. In the case of sucrose the values of D varied widely from one sampling time to another, that is, from 2 to 4 to 6 hours. This can be seen in table 6. For example, for 50°C there is one order of magnitude difference between the diffusion coefficient for 2 hours (1.5×10^{-8} cm^2 sec^{-1}) and for 6 hours (1.6×10^{-7} cm^2 sec^{-1}).

The possible existance of a significant surface resistance for sucrose transport into the sample was investigated making the calculations assuming steady state mass transfer. Considering that the magnitude of the change of sucrose concentration within the sample was small (between 15 and 315 mg sucrose/ g H_2O) as compared with the sucrose concentration in the osmotic solution (1500 mg/ g H_2O), and that the sucrose flux remains close to constant throughout the process (table 7) the assumption is, if

obviously not true, a good approximation. The actual sucrose concentration gradient is calculated on base of the mean concentration value defined as follows:

$$\overline{\Delta C} = C_1 - \frac{C_f - C_o}{2} \qquad (4\text{-}1)$$

where $\overline{\Delta C}$ = mean sucrose concentration gradient

C_1 = concentration of sucrose in the solution

C_f = final concentration of sucrose in the sample

C_o = initial concentration of sucrose in the sample.

Thus, using the general mass transfer equation (3-3) as well as equation (3-4), sucrose uptake data were calculated and the results are expressed in table 7 where the experimental data proved to fit the model given very close film mass transfer coefficient values for a given temperature regardless of the sampling time for which the calculation was made.

The value of each mass transfer coefficient increases with process temperature and decreases with viscosity. The inverse of the mass transfer coefficient, namely the mass transfer resistance, and the viscosity have a correlation coefficient of 0.993, which indicates the dependence of sucrose transport on the viscosity of the solution. Similar situation was found by Chandrasekaran and King (1972) for the diffusion coefficient of individual sugars and dilute organic species in ternary systems being water the third component. They obtained results indicating that the activation energy for the sugar diffusion coefficient is approximately equal to that for the viscosity of the solution, but is greater than that for the organic species at high sucrose concentrations. Hence, the viscosity of the solution can be used as a parameter for correlating the sugar

diffusion coefficient as a function of temperature by postulating that the group $D\mu/T$, where μ is viscosity , is constant.

Plotting the log of the film coefficient versus the inverse of the absolute temperature it is possible to observe that the relation between 25 and 40°C is linear following the Arrhenius equation (Figure 9), however between 40 and 60°C the slope seems to undergo a change, giving a higher value of energy of activation. This suggests that at this temperature range, besides viscosity, other temperature-dependent factors as kinetic energy start having a higher and significantly contribution on the overall scheme. The energy of activation for the region between 25 and 50°C is 7 Kcal/mole and for the 50 to 60°C region is 13 Kcal/mole.

At sufficiently low solution viscosity and depending on the model one is working with, solids uptake can follow Fick's second law for unidirectional transport as in the case of NaCl uptake during cheese salting reported by Geurts et. al. (1974).

In addition to viscosity, there is another factor which can play a role in the transport of sucrose, either across the surface film or through the apple tissue, namely the large difference between the flux of water migrating from the sample and the flux of sucrose getting into the sample. The quantitative relationship between the two can be of the order of 45 to 1, respectively, on an average basis. In addition, the flux of water must carry along soluble low molecular weight substances, for example glucose, fructose, organic acids and others with which sucrose, with a molecular weight about twice as large as that of glucose competes for the same pathways.

Because in our model the surface film seems to have a large effect there is a fairly even distribution of sucrose concentration within the

apple tissue. The corresponding theoretical distribution can not be readily calculated because boundary conditions (including the true external sucrose concentration) are unknown. It is also unknown if this concentration changes with time or not.

The observations were made in a system using only 60 % sucrose solutions. With different concentrations or different solutes the character of the controlling mechanism (s) could be different.

The finding of a sucrose distribution throughout apple samples presenting a concentration profile from the surface to the center is in contrast to results of Lee and Selunkhe (1968) who used autoradiographic techniques. In their studies the sucrose remains within the surface layers of the apple samples. The conditions the authors report are sucrose solutions 23 and 50 % concentrated as well as dry sugar, room temperature and process times of 5 to 50 hours.

4.2. Optimization of conditions for osmotic preconcentration of fruit pieces prior to freeze dehydration.

The present section discusses the use of different osmotic agents under different process conditions, namely temperature, concentration and method of contacting (with or without vacuum). Two main factors are considered: water removal and increase of solids content, as an optimal combination of them is desirable to have a suitable material for further freeze dehydration with the aim of preserving the highest possible organoleptic quality of the final product which is either to be eaten dry, or rehydrated.

4.2.1. Water removal.

The percentage of initial moisture content of osmotically

dehydrated apple samples for different solutions at different process conditions is shown in table 8 and the actual moisture content expressed in g H_2O / g sample in table 9 for each of the sampling times. Figures 10 and 11 are graphical examples from table 8 in which the percentage of initial moisture content is plotted versus time.

Since it was shown that the osmotic dehydration of samples follows Fick's second law for a system using 60 % sucrose the data were treated as if in all cases the controlling transport mechanism of water is diffusion. Thus, a diffusion coefficient for each set of conditions was obtained (Table 10).

The diffusion coefficients increase with temperature, as expected (for 60 % sucrose Ea was 12 Kcal/mole) and moderate increases in the process temperatures can bring about substantial increases in the diffusion coefficients. For example, for 50 % sucrose solution system without vacuum contacting (Table 10) the calculated water diffusion coefficient at 30°C is 3.5×10^{-6} cm^2 sec^{-1} and at 40°C is 1.13×10^{-5} cm^2 sec^{-1}.

The ideal case of transport of water in which diffusion is the controlling factor from a solid cylinder and the initial moisture concentration is uniform and in which the concentration at the surface remains constant with time is quantitatively described by equations (2-2), (2-3) and (2-4). These equations clearly show that the rate of water removal strongly depends on the value of the diffusion coefficient.

Comparing different treatments, for 25 % solutions without vacuum contacting, sucrose gave the highest diffusion coefficient at any temperature as compared with lactose and whey. The differences were around 1.5 to 2 fold. In the case of whey solutions, the presence of protein probably interfered with the contact between the sample and the osmotic solution.

For the case in which vacuum contacting was used, no significant difference was noticed. This could mean that the reason for the differences noticed in the "no-vacuum" system is that the sucrose solution is able to get close to the apple cell membranes so establishing more rapidly and effectively the activity gradient. This effect is overcome if the vacuum contacting step is performed, so having about the same water diffusion coefficients.

For the 50 % solutions without vacuum the differences followed about the same pattern showed by the 25 % solutions. The sucrose-whey system gave slightly lower values for the diffusion coefficient. For the case in which vacuum contacting operation was applied the behaviour was almost identical, but the differences were still smaller. For example, for 40°C, the sucrose solution gave after 6 hours of process a product with 61.27 g H_2O / 100 g sample, and the 50 % sucrose/whey solution gave a final concentration of 65.03 g H_2O / 100 g sample.

4.2.2. Solids content.

The change of solids content expressed as g solids/g sample is a function of two different but related effects. Firstly, water removal reduces the total weight of the sample and therefore increases the relative value of solids content. Secondly, there is a net increase in the absolute weight of solids in the sample due to the solids uptake as described in table 11 in which the percentage of initial solids content is presented for all systems. Similarly, table 12 contains the relative solids concentration (g solids / 100 g sample) of the samples. Example of this information can be seen in figure 12.

The uptake of osmotic agents can be of great importance as their taste will be present in the final product. This is specially evident for

the case of sweet solutes as sucrose.

Hawkes and Flink (1976) showed that a plot of normalized solids content versus $(\text{time})^{\frac{1}{2}}$ gives a linear relationship as described before in section 3.4.3., where k = mass transfer coefficient for the particular system. An illustration os a NSC versus $(\text{time})^{\frac{1}{2}}$ from which the k value was obtained is presented in figure 13 and the k values are shown in table 13.

The increase in temperature definitively brings about an increase on the value of k. When the k values are plotted versus temperature (°C) the relations are occasionally linear.

The most important effect is for the 50 % solutions for which for a 10°C increase in the process temperature produces an increase in the value of k of about 80 %. Figure 14 graphically exemplifies this relationship. This becomes important if we remember that one of the quantitative aims of the osmotic operation is to preconcentrate the sample to about 25 to 30 % solids.

The concentration of the osmotic solution is also important as far as the k value is concerned. The increase for the k value by using a 50 % sucrose solution instead one 25 % concentrated is about 100 % for any temperature.

For the 25 % solutions without vacuum contacting step, again sucrose was the most effective. The explanation for this is rather complex as it combines the ability of the solution to remove water, as well as penetrate into the sample. In any event, it is clear that the protein and the fat present in the cheese whey can prevent the migration of lactose and of other low molecular weight compounds into the apple tissue. For the system in which vacuum contacting was used there were not appreciable differences among the k values for the different solutions.

The k value showed no significant difference among the 50% solutions when no vacuum contacting operation was used. When it was used, the sucrose solution scored higher than the combinations sucrose/lactose or sucrose/whey.

Giving a requirement of osmotically treated product with 25 to 30 % solids, any treatment with the 50 % solutions is capable of achieving that condition in less than 6 hours. If 25 % solutions are used, there are some conditions under which the solids concentration requirement is also met, for example, 6 hours at 40°C with 25 % sucrose solution, 5 hours at 30°C with 25 % lactose solution using the vacuum contacting step, or 6 hours at 50°C with 25 % whey solution.

4. 3. Organoleptic evaluations.

A Hedonic scale with 9 points, from 1 = dislike extremely to 9 = like extremely was used for 12 people and the computation of the data was made by analysis of variance according with Ellis (1966). The results are presented in table 14.

For taste, the samples treated with a 50 % solution made of the combination sucrose/whey at 25°C and with vacuum contacting gave the highest score. It was higher than those processes in which, for the same solution, no vacuum contacting took place, or a higher process temperature was used and also higher than the score obtained by the 50 % sucrose solution at 25°C. The lowest score was for the system in which a 25 % whey solution at 50°C was used. In general, it can be seen that the organoleptic acceptance of the product is relatively good for those systems in which cheese whey was used combined with sucrose on an equal proportion bases. If used alone, it proved to have low acceptance.

As far as texture is concerned, the scores were similar to those of taste, mainly for the top scores. Again, the system 50 % sucrose/whey at

25°C with vacuum contacting obtained the highest scores followed by 50 % sucrose at 25°C.

4.4. Microbial determinations

In any count plate determination the total number of colonies was higher than 30, being practically no difference between fresh prepared and after processing solutions of sucrose, lactose, cheese whey or any of the combinations, which indicates that the operation conditions do not favor microbial growth, doubtlessly because of the extremely high osmotic pressure microorganisms can not resist (Stanier et. al.).

5. CONCLUSIONS

Osmotic dehydration of apples is a process on which many factors affect its efficiency in terms of mass transfer and final general quality of the product. One of the aims of this research was to find the best process conditions to preconcentrate apple pieces to a 25 to 30 % solids concentration and subject them later to freeze drying, hoping to preserve by the use of this sequence of operations most of the original quality characteristics of the product.

The general conclusions of this research were:

a.) The mechanism of water removal from the apple pieces is diffusion-controlled and the relationship between the diffusion coefficient and the temperature follows the Arrhenius equation, giving a energy of activation of about 12 Kcal/mole for osmotic treatment in 60 % sucrose solution. The calculated diffusion coefficients do take into consideration the shrinkage of the sample by using mean values for the radius of the cylinders calculated with the radius of the fresh cylindrical sample and of the processed sample. For the calculations of the mean distances from the surface of the cylinder to a certain depth, the original distance was multiplied by a correction factor which was the ratio

$$\frac{\text{diameter after processing}}{\text{diameter of fresh sample.}}$$

This approach is evidently empirical, but is closer to the real system than just using the dimensions of the fresh apple sample. In order to have the true diffusion coefficients, the change of dimentions with respect to time should be considered in the fundamental equations describing the diffusion phenomenon.

As this is not the case, the true coefficients would therefore be somewhat different from the reported values.

b.) The mechanism of net sucrose uptake behaves as if it were regulated by a surface resistance the magnitude of which depends on the viscosity of the osmotic solution. When the viscosity is low enough, the mobility of the solute molecules has an important effect on the process. In the specific case of a 60 % sucrose solution between 50 and 60°C the kinetic energy of the sucrose molecules seems to be high enough to start significantly contributing to the transfer of the solutes into the sample.

c.) Within the apple tissue sucrose molecules keep distributing themselves toward the inner part of the sample ending up with a decreasing concentration profile from the surface to the center of the apple cylinder.

d.) The vacuum contacting operation proved to increase the value of both water diffusion coefficient and of solids uptake mass transfer coefficient. The significance of this improvement remains to be investigated in terms not only of mass transfer characteristics and organoleptic quality of the product, but also, very importantly, from the energy consumption standpoint.

e) Under any of the studied conditions, any one of the three 50 % solutions provides enough driving force to remove water from and add solids to the sample to achieve the specific conditions for freeze drying. The processing time can be reduced depending on the required final product characteristics, equipment available and osmotic solute disponibility.

f.) It is possible to obtain a product with a required solids concentration (25 - 30 %) using 25 % solutions if the required process

conditions, namely temperature and/or vacuum contacting operation are used.

g.) Cheese whey was a satisfactory osmotic medium when combined with sucrose. This combination has economic advantages due to the difference in price between the two materials. For the Boston area, the price per pound of sugar is $0.26 and the price for food cheese whey (spray dried) is $ 0.18

h.) The use of 50 % solution of cheese whey/sucrose at 25°C gives better taste and texture to the osmotically preconcentrated freeze dried rehydrated samples than any other solution, including 50 % sucrose solution. Increase in the temperature of the osmotic operation seems to have a deleterious effect on both taste and texture of the final rehydrated product.

i.) The high osmotic pressure of the solutions excludes the possibility of microbial growth during the osmotic operation regardless of the rest of the conditions.

Table 1. Hardness of apple samples determined with the Instron Universal Testing Instrument model 1122[a]

Batch #	Force[b] (g force)	Standard deviation (g force)
1	5.23	0.19
2	5.52	0.05
3	5.48	0.21
4	5.57	0.16
5	5.61	0.11

a - experimental conditions explained in section 3.1.1.

b - average of five determinations

Table 2. Moisture content (w/w %) of the different concentrinc rings from the apple cylinders osmotically treated at different times and temperatures using 60 % sucrose solution[a].

Time (hr)	Temp. (°C)	Ring number[b] 1	2	3	4	whole cross section
6	25	71.09	82.71	83.95	84.18	78.00
	40	50.70	72.69	83.98	84.09	72.90
	50	50.11	65.00	75.91	81.54	67.50
	60	49.84	65.10	70.55	75.28	62.59
4	25	71.84	83.70	84.07	84.62	79.37
	40	55.22	82.05	84.96	85.25	76.35
	50	53.15	75.38	82.46	84.62	72.51
	60	50.28	68.74	16.02	80.00	66.87
2	25	76.18	85.35	85.44	85.47	81.51
	40	65.53	83.59	85.87	86.88	80.12
	50	67.97	81.36	85.16	86.21	78.18
	60	63.68	79.60	83.55	84.48	73.96

a - the original distances from the center of the cylinder to the mean thickness of each ring are:
Ring 1 : 0.14 cm
Ring 2 : 0.43 "
Ring 3 : 0.72 "
Ring 4 : 0.98 "

b - average value of two determinations.

Table 3. Calculated diffusion coefficients of water migrating from apple samples during osmotic treatment with 60 % sucrose solution at different temperatures.

Temp. (°C)	Time (hr)	C^a_{corr} w/w %	E^b	Dt/a^2	a^2 (cm^2)	D ($cm^2\ sec^{-1}$)
60	6	63.13	0.492	0.064	0.9882	2.93×10^{-6}
60	4	67.38	0.583	0.041	1.0040	2.85×10^{-6}
60	2	74.40	0.732	0.014	1.1000	2.13×10^{-6}
50	6	68.00	0.596	0.039	1.0380	1.87×10^{-6}
50	4	72.97	0.701	0.019	1.0870	1.43×10^{-6}
50	2	78.57	0.821	0.005	1.1170	0.85×10^{-6}
40	6	73.55	0.710	0.017	1.0600	8.50×10^{-7}
40	4	76.76	0.782	0.008	1.1270	6.60×10^{-7}
40	2	80.48	0.861	0.003	1.1660	5.18×10^{-7}
25	6	78.39	0.817	0.006	1.1600	3.20×10^{-7}
25	4	79.76	0.846	0.004	1.1230	3.12×10^{-7}
25	2	81.85	0.890	0.001	1.2590	2.90×10^{-7}

a - correction: calculation of water concentration= (g H_2O)/(g H_2O) + (g soluble solids)

b - $E = (C_{corr} - C_1)/(C_o - C_1)$

where: C_o = Initial sucrose concentration in the apple = 87 %

C_1 = Water concentration of the solution = 40 %

Table 4. Data used in calculation of the theoretical water concentration of osmotically treated apple samples.

Temp. (°C)	Time hr	Ring no.	r_o[a] (cm)	f[b]	a_f[c] (cm)	r_1[d] (cm)	D[e] $\frac{cm^2}{sec}$	a_f^2 (cm^2)	$\frac{D\,t}{a_f^2}$	$\frac{r_1}{a_f}$	$\frac{C'-C_1}{C_o-C_1}$[f]	C' %	C_{real} %	Diff.[g]
60	6	1	0.9887	0.9413	0.994	0.930	2.5×10^{-6}	0.988	0.054	0.93	0.85	47.05	49.84	-5
60	6	2	0.7239	"	"	0.681	"	"	"	0.68	0.40	68.20	61.10	10
60	6	3	0.4388	"	"	0.413	"	"	"	0.41	0.11	81.83	70.55	14
60	6	4	0.1403	"	"	0.132	"	"	"	0.13	0.02	85.96	75.28	12
60	4	1	0.9887	0.9448	1.000	0.934	"	0.892	0.040	0.93	0.84	47.52	50.28	-5
60	4	2	0.7239	"	"	0.683	"	"	"	0.68	0.32	71.96	68.74	4
60	4	3	0.4388	"	"	0.414	"	"	"	0.41	0.06	84.18	76.02	10
60	4	4	0.1403	"	"	0.132	"	"	"	0.13	0.01	86.53	80.00	8
60	2	1	0.9887	0.9657	1.049	0.954	"	0.932	0.019	0.91	0.65	56.45	63.68	-11
60	2	2	0.7239	"	"	0.699	"	"	"	0.66	0.11	81.83	79.60	3
60	2	3	0.4388	"	"	0.423	"	"	"	0.40	0.005	86.76	83.55	4
60	2	4	0.1403	"	"	0.135	"	"	"	0.12	h	87.00	84.48	3
50	6	1	0.9887	0.9524	1.019	0.941	1.4×10^{-6}	0.907	0.034	0.92	0.82	48.46	50.11	-3
50	6	2	0.7239	"	"	0.689	"	"	"	0.67	0.26	74.78	65.0	13
50	6	3	0.4388	"	"	0.417	"	"	"	0.41	0.04	85.12	75.91	11
50	6	4	0.1403	"	"	0.133	"	"	"	0.12	h	87.00	85.84	6
50	4	1	0.9887	0.9586	1.033	0.9487	"	0.918	0.022	0.91	0.66	55.98	53.15	5
50	4	2	0.7239	"	"	0.6930	"	"	"	0.67	0.12	81.12	75.38	7
50	4	3	0.4388	"	"	0.420	"	"	"	0.40	0.005	86.76	82.43	5
50	4	4	0.1403	"	"	0.134	"	"	"	0.13	h	87.00	84.62	3
50	2	1	0.9887	0.9693	1.057	0.958	"	0.939	0.011	0.90	0.50	63.50	67.97	-7
50	2	2	0.7239	"	"	0.7017	"	"	"	0.66	0.02	86.06	81.36	5
50	2	3	0.4388	"	"	0.4253	"	"	"	0.40	h	87.00	85.16	2
50	2	4	0.1403	"	"	0.1360	"	"	"	0.12	h	87.00	86.21	1

Table 4. Data used in calculation of the theoretical water concentration of osmotically treated apple samples.

Temp. (°C)	Time hr	Ring no.	r_o^a (cm)	f^b	a_f^c (cm)	r_1^d (cm)	D^e $\frac{cm^2}{sec}$	a_f^2 (cm^2)	$\frac{D\,t}{a_f^2}$	$\frac{r_1}{a_f}$	$\frac{C'-C_1^f}{C_o-C_1}$	C' %	C_{real} %	Diff.[g]
40	6	1	0.988	0.914	1.03	0.904	8.0×10^{-7}	1.06	0.016	0.878	0.47	64.91	50.70	22
40	6	2	0.723	"	"	0.662	"	"	"	0.643	0.06	84.18	72.69	14
40	6	3	0.438	"	"	0.401	"	"	"	0.389	h	87.00	83.98	3
40	6	4	0.140	"	"	0.128	"	"	"	0.124	h	87.00	84.09	3
40	4	1	0.988	0.971	1.06	0.960	"	1.127	0.010	0.904	0.50	63.50	55.22	13
40	4	2	0.723	"	"	0.703	"	"	"	0.662	0.02	86.06	82.05	5
40	4	3	0.723	"	"	0.426	"	"	"	0.401	h	87.00	84,96	2
40	4	4	0.140	"	"	0.136	"	"	"	0.123	h	87.00	85.25	2
40	2	1	0.988	0.979	1.08	0.968	"	1.166	0.040	0.896	0.32	61.96	65.33	9
40	2	2	0.723	"	"	0.709	"	"	"	0.656	h	87.00	83.59	4
40	2	3	0.438	"	"	0.429	"	"	"	0.398	h	87.00	85.87	1
40	2	4	0.140	"	"	0.137	"	"	"	0.127	h	87.00	86.88	1
25	6	1	0.988	0.978	1.07	0.967	3.1×10^{-7}	1.159	0.005	0.897	0.32	71.96	71.09	1
25	6	2	0.723	"	"	0.708	"	"	"	0.657	h	87.00	82.71	5
25	6	3	0.438	"	"	0.429	"	"	"	0.398	h	87.00	83.95	4
25	6	4	0.140	"	"	0.137	"	"	"	0.117	h	87.00	84.18	3
25	4	1	0.988	0.993	1.11	0.981	"	1.23	0.003	0.884	0.12	81.36	71.48	12
25	4	2	0.723	"	"	0.718	"	"	"	0.647	h	87.00	83.70	4
25	4	3	0.438	"	"	0.435	"	"	"	0.392	h	87.00	84.07	3
25	4	4	0.140	"	"	0.139	"	"	"	0.125	h	87.00	84.42	3
25	2	1	0.988	0.998	1.12	0.986	"	1.25	0.001	0.879	0.05	84.65	76.18	10
25	2	2	0.723	"	"	0.722	"	"	"	0.643	h	87.00	85.35	2
25	2	3	0.438	"	"	0.438	"	"	"	0.390	h	87.00	85.44	2
25.	2	4	0.140	"	"	0.140	"	"	"	0.124	h	87.00	85.47	2

a - r_o=distance from the center of the cylinder to the mean thickness of each ring.
b - f_o= shrinkage correction factor for r_o.

Table 4.

(continuation) Data used in calculation of the theoretical water concentration of osmotically treated apple samples.

a - r_o = distance from the center of the cylinder to the mean thickness of each ring.

b - f = shrinkage correction factor for r_o. $f = 1 - a_f/2a_o$

where a_f = final radius of the cylinder

a_0 = initial radius of the cylinder

c - a_f was above explained.

d - $r_1 = (r_o)(f)$

e - D values were taken from the regression fitted straigth line obtained for the log D vs 1/T relationship

f - C' = water concentration (%) in the sample at time = t
C_o = " " " " " " " time = 0

C_1 = " " " of the solution

g - If sign is (-), $C' < C_{real}$

h - E value tends to zero, thus C' tends to C_o

Table 5. Sucrose content of different concentric rings from apple cylinders osmotically treated at different times and temperatures using 60 % sucrose solution (mg sucrose/ g H_2O) [a]

Time (hr)	Temp. (°C)	Ring number [b] 1	2	3	4	whole cross section
6	25	195.60	114.66	57.46	12.28	103.23
	40	423.75	160.50	63.00	14.30	161.00
	50	592.55	180.40	77.95	25.82	227.00
	60	415.92	278.00	204.00	164.50	315.00
4	25	117.85	19.25	13.85	9.05	52.00
	40	236.00	51.50	22.50	21.00	86.00
	50	425.50	74.00	32.50	28.00	138.50
	60	301.00	201.00	140.00	96.00	183.00
2	25	16.40	14.65	14.65	14.65	15.35
	40	67.97	20.00	19.80	26.75	50.00
	50	197.65	28.00	25.00	25.00	52.97
	60	160.52	99.50	56.10	35.00	67.42

Table 6. Calculated diffusion coefficient of sucrose going into the apple samples during osmotic treatment with 60 % sucrose solution.

Temp. (°C)	Time (hr)	$\bar{C}$ mg suc / g H_2O	E	a (cm)	a^2 (cm^2)	Dt/a^2	D $cm^2\ sec^{-1}$
60	6	315.00	0.796	0.994	0.988	0.007	3.2×10^{-7}
60	4	183.00	0.885	1.002	1.004	0.002	1.3×10^{-7}
60	2	87.42	0.949	1.049	1.100	0.0005	0.76×10^{-7}
50	6	227.00	0.856	1.019	1.038	0.0035	1.6×10^{-7}
50	4	138.50	0.915	1.033	1.087	0.001	0.7×10^{-7}
50	2	52.97	0.972	1.057	1.117	0.0001	0.1×10^{-7}
40	6	161.00	0.999	1.030	1.060	0.0012	5.8×10^{-8}
40	4	86.00	0.950	1.062	1.127	0.0005	3.9×10^{-8}
40	2	26.75	0.990	1.080	1.166	0.0001	1.6×10^{-8}
25	6	103.23	0.939	1.077	1.160	0.0003	1.6×10^{-8}
25	4	52.00	0.913	1.110	1.123	0.0001	0.7×10^{-8}
25	2	15.35	0.998	1.122	1.259	0.0	-

Table 7. Film mass transfer coefficient of sucrose (k_f) penetrating apple samples during osmotic treatment ($cm^2\ sec^{-1}$).

Temp. (^oK)	Time (hr)	C_f[a] mg suc / g H_2O	weight sample (g)	x_{H_2O}[b]	surface area (cm^2)	$\overline{\Delta C}$[c] mg suc / g_{H_2O}	Flux[d] g suc / hr cm^2	k_f[e] cm/hr	$\bar{k}_f$[f] cm/hr	$1/\bar{k}_f$ hr/cm	μ soln. (poises)
333	0	-	-	0.87	-	-	-	-			
333	2	87.00	0.92	0.74	2.12	1450.10	12.04	0.0083			
333	4	183.00	0.98	0.67	2.19	1402.50	12.79	0.0091	0.0091	109.89	9.5
333	6	315.00	0.92	0.62	2.13	1336.50	13.72	0.0100			
323	0	-	-	0.87	-	-	-	-			
323	2	53.00	0.99	0.78	2.28	1479.50	6.96	0.0047			
323	4	138.00	1.17	0.72	2.69	1437.00	9.43	0.0069	0.0050	200.00	18.0
323	6	322.00	0.82	0.67	3.10	1392.50	4.84	0.0034			
313	0	-	-	0.87	-	-	-	-			
313	2	26.00	1.21	0.80	2.78	1493.00	2.44	0.0016			
313	4	86.00	1.21	0.72	2.79	1463.00	5.84	0.0039	0.0036	277.70	21.0
313	6	161.00	1.42	0.73	3.28	1425.50	7.86	0.0055			
298	0	-	-	0.87	-	-	-	-			
298	2	15.00	3.44	0.81	7.91	1498.50	0.53	0.00035			
298	4	52.00	1.97	0.79	4.54	1480.00	3.44	0.0023	0.0020	500.00	44.0
298	6	103.00	2.79	0.78	6.43	1454.50	5.14	0.0035			

Table 7.
(continuation).

a - average concentration of whole cross sections

b - weight fraction of water in sample : g H_2O/g sample

c - Average concentration gradient = $C_1 - (C_f - C_o)/2$

where C_f = sucrose conc. at time = t

C_o = sucrose concentration at time = 0

= 12 mg/g H_2)

C_1 = sucrose concentration in the osmotic solution,(1500 mg suc/g H_2O).

d - Flux = $(C_f - C_o)$(Wt. sample)(x_{H_2O}) / (t) (A)

e - k_f = flux/$\overline{\Delta C}$

f - average for different times

Table 8. Percentage of initial moisture content of osmotically dehydrated apple cylinders

Osmotic solution	Temp. (°C)	Time (hours) 0.0	0.5	1.0	2.5	5.0	6.0
25 % sucrose	25	100.00	96.01	92.96	91.99	83.99	78.45
	30	100.00	91.66	90.02	83.50	73.50	73.28
	40	100.00	93.98	88.93	78.60	68.73	62.06
	50	100.00	87.99	82.04	72.85	63.80	58.20
50 % sucrose	25	100.00	87.65	81.94	76.94	61.92	58.04
	30	100.00	86.20	77.63	63.88	46.90	43.20
	40	100.00	86.01	78.89	61.11	39.78	29.88
	50	100.00	75.55	61.07	46.97	30.42	24.00
25 % lactose	25	100.00	84.22	96.00	92.83	90.41	86.09
	30	100.00	96.81	93.06	94.29	83.00	82.00
	40	100.00	94.91	92.15	88.88	82.51	78.83
	50	100.00	84.34	96.63	83.00	73.00	73.28
25 % whey	25	100.00	-	95.22	91.14	86.66	71.94
	30	100.00	94.72	94.83	91.71	85.19	85.30
	40	100.00	92.80	91.16	81.93	73.61	63.95
	50	100.00	92.04	81.42	67.10	58.76	54.47
50 % suc/lac	25	100.00	87.31	81.47	70.41	65.11	-
	30	100.00	85.83	79.06	60.74	50.33	45.07
	40	100.00	82.53	74.60	41.30	37.24	-
	50	100.00	78.41	70.27	36.38	28.99	-
50 % suc/whey	25	100.00	88.57	87.79	73.70	66.72	73.95
	30	100.00	89.45	85.68	70.25	65.31	57.00
	40	100.00	88.71	81.51	69.28	58.16	53.34
	50	100.00	84.85	68.16	47.96	34.26	22.74

Table 8. (contn.) Percentage of initial moisture content of osmotically dehydrated apple cylinders [a]

Osmotic solution	Temp. (°C)	Time(hr) 0.0	0.5	1.0	2.5	5.0	6.0
25 % sucrose	25	100.00	112.27	109.32	104.74	98.96	61.64
	30	100.00	124.06	119.29	122.23	118.20	117.12
	40	100.00	116.71	114.54	107.61	109.12	109.21
	50	100.00	104.16	106.69	95.10	79 31	74.40
50 % sucrose	25	100.00	93.84	92.03	72.27	65.06	61.78
	30	100.00	91.80	84.11	70.38	61.49	64.76
	40	100.00	89.56	68.41	72.53	52.61	49.38
	50	100.00	85.29	67.00	38.63	28.26	27.50
25 % lactose	25	100.00	119.76	127.77	123.06	121.22	113.80
	30	100.00	120.79	112.53	113.23	108.77	93.56
	40	100.00	122.80	120.66	112.00	101.93	95.89
	50	100.00	119.81	117.21	114.49	81.87	-
25 % whey	25	100.00	98.77	94.91	86.79	62.16	91.71
	30	100.00	97.10	95.40	87.61	96.95	89.94
	40	100.00	97.51	96.15	86.73	74.51	78.90
	50	100.00	99.71	92.08	81.75	74.61	70.62
50 % suc/lac	25	100.00	92.72	85.75	71.67	54.87	53.00
	30	100.00	85.55	85.08	75.05	51.13	41.43
	40	100.00	92.63	83.05	51.85	40.64	32.68
	50	100.00	80.66	71.27	47.02	45.80	26.35
50 % suc/whey	25	100.00	85.34	79.81	72.34	65.13	62.22
	30	100.00	87.10	80.57	64.81	53.71	40.96
	40	100.00	84.07	81.51	66.76	48.43	45.14
	50	100.00	82.58	62.73	45.27	31.71	31.50

a - samples held to vacuum prior to contacting with osmotic solution.

Table 9. Moisture content of osmotically treated apple samples (g H_2O / 100 g sample)

Osmotic solution	Temp. (°C)	Time (hr) 0.0	0.5	1.0	2.5	5.0	6.0
25 % sucrose	25	86.20	84.35	84.00	82.57	81.00	80.28
	30	86.20	83.46	86.70	82.39	75.59	77.58
	40	86.20	85.45	84.48	77.75	75.97	73.50
	50	86.20	83.39	81.04	75.85	70.35	68.02
50 % sucrose	25	86.20	80.81	78.50	77.10	73.04	72.47
	30	86.20	83.43	78.02	74.60	67.83	-
	40	86.20	79.40	77.48	72.04	63.49	51.32
	50	86.20	75.18	69.55	65.78	54.65	49.26
25 % lactose	25	86.20	79.84	81.99	84.34	82.90	82.45
	30	86.20	84.34	84.47	82.57	80.44	81.19
	40	86.20	83.84	83.32	82.73	81.82	81.46
	50	86.20	85.42	83.90	-	77.03	-
25 % whey	25	86.20	84.05	84.77	82.78	82.16	82.42
	30	86.20	84.10	84.69	83.19	82.90	82.66
	40	86.20	85.52	84.09	82.79	79.48	79.24
	50	86.20	84.70	83.15	79.22	76.79	76.35
50 % suc/lac	25	86.40	80.32	78.18	77.14	72.96	-
	30	86.40	80.39	78.79	73.64	69.29	67.08
	40	86.40	76.01	74.07	62.70	59.19	-
	50	86.40	76.86	74.43	57.82	54.25	-
50 % suc/whey	25	86.73	79.37	78.93	73.76	72.97	71.80
	30	86.73	80.49	79.57	73.76	72.20	70.82
	40	86.73	81.16	78.39	74.37	69.19	67.18
	50	86.73	79.35	74.44	67.43	56.95	47.76

Table 9.

(continuation) Moisture content of osmotically treated apple samples (g H_2O / 100 g sample)[a]

Osmotic solution	Temp. (°C)	Time (hr) 0.0	0.5	1.0	2.5	5.0	6.0
25 % sucrose	25	86.20	84.42	83.84	83.08	82.02	71.13
	30	86.20	82.63	81.11	79.85	79.57	78.59
	40	86.20	81.36	81.28	79.85	78.06	76.55
	50	86.20	83.51	82.29	78.85	72.06	70.94
50 % sucrose	25	86.20	77.65	75.59	73.26	70.18	69.20
	30	86.20	78.99	76.29	72.18	69.77	67.18
	40	86.20	77.02	69.55	68.55	65.52	61.27
	50	86.20	75.89	71.74	56.05	46.18	43.79
25 % lactose	25	86.40	81.67	81.21	81.15	78.86	79.19
	30	86.40	81.00	73.34	77.71	74.74	74.30
	40	86.40	81.31	79.37	76.93	74.68	73.38
	50	86.40	79.97	78.75	75.42	72.79	75.71
25 % whey	25	86.73	81.73	82.66	78.69	56.95	-
	30	86.73	84.20	83.64	78.69	72.83	86.00
	40	86.73	82.82	82.51	80.96	78.07	77.97
	50	86.73	82.27	81.42	75.77	77.45	75.13
50 % suc/lac	25	86.40	78.05	76.76	71.09	67.77	64.49
	30	86.40	78.22	76.65	69.35	64.33	58.73
	40	86.40	76.45	73.00	62.62	53.94	50.38
	50	86.40	75.22	70.78	58.63	38.43	45.32
50 % suc/whey	25	86.73	78.46	78.04	75.82	72.46	70.84
	30	86.73	78.61	77.13	72.13	68.47	63.57
	40	86.73	79.03	77.13	73.78	63.17	65.03
	50	86.73	78.51	72.31	66.34	55.32	53.01

a - samples held to vacuum prior to contacting with osmotic solution

Table 10. Diffusion coefficient of water leaving apple samples during osmotic treatment (cm^2 sec^{-1}).

Without vacuum step operation

Osmotic solution	Temperature (°C)	$\bar{D}^a$ (cm^2 sec^{-1})
25 % sucrose	25	3.89×10^{-6}
	30	1.55×10^{-5}
	40	1.47×10^{-5}
	50	2.90×10^{-5}
50 % sucrose	25	2.58×10^{-6}
	30	3.50×10^{-6}
	40	1.13×10^{-5}
	50	1.80×10^{-5}
25 % lactose	25	1.94×10^{-5}
	30	5.68×10^{-6}
	40	4.19×10^{-6}
	50	7.60×10^{-6}
25 % whey	25	2.70×10^{-6}
	30	2.26×10^{-6}
	40	4.20×10^{-6}
	50	1.30×10^{-5}
50 % suc/lac	25	3.10×10^{-6}
	30	4.00×10^{-6}
	40	1.49×10^{-5}
	50	1.92×10^{-5}
50 % suc/whey	25	3.74×10^{-6}
	30	3.47×10^{-6}
	40	3.87×10^{-6}
	50	1.07×10^{-5}

With vacuum step operation

Osmotic solution	Temperature (°C)	$\bar{D}^a$ (cm^2 sec^{-1})
25 % sucrose	25	2.85×10^{-6}
	30	1.33×10^{-5}
	40	2.00×10^{-5}
	50	1.36×10^{-5}
50 % sucrose	25	5.60×10^{-6}
	30	5.96×10^{-6}
	40	1.13×10^{-5}
	50	2.21×10^{-5}
25 % lactose	25	1.59×10^{-5}
	30	3.72×10^{-5}
	40	4.06×10^{-5}
	50	5.60×10^{-5}
25 % whey	25	2.32×10^{-5}
	30	1.13×10^{-5}
	40	1.34×10^{-5}
	50	3.40×10^{-5}
50 % suc/lac	25	6.44×10^{-5}
	30	8.80×10^{-6}
	40	2.29×10^{-5}
	50	2.12×10^{-5}
50 % suc/whey	25	4.32×10^{-5}
	30	6.34×10^{-6}
	40	6.60×10^{-6}
	50	1.66×10^{-5}

a - average diffusion coefficient from calculation at different processing times.

Table 11. Percentage of initial solids content of osmotically treated apple samples

Osmotic solution	Temp. (°C)	Time (hr) 0.0	0.5	1.0	2.5	5.0	6.0
25 % sucrose	25	100.00	111.36	110.60	121.30	123.17	120.35
	30	100.00	113.87	117.72	111.56	148.29	132.28
	40	100.00	100.02	102.10	140.15	135.84	139.77
	50	100.00	109.49	119.93	144.85	167.45	170.97
50 % sucrose	25	100.00	130.00	140.14	142.76	142.76	137.78
	30	100.00	107.00	136.60	135.86	139.00	-
	40	100.00	139.46	143.22	148.25	142.90	177.02
	50	100.00	155.81	167.07	152.60	157.61	154.44
25 % lactose	25	100.00	132.86	112.51	107.70	116.53	114.42
	30	100.00	112.01	106.80	124.36	126.09	118.75
	40	100.00	113.71	115.32	116.06	114.52	112.03
	50	100.00	89.91	115.80	-	135.96	119.26
25 % whey	25	100.00	136.46	106.82	118.43	117.51	95.86
	30	100.00	111.82	107.12	115.73	109.76	111.78
	40	100.00	98.12	104.74	106.36	118.72	104.63
	50	100.00	103.85	103.03	109.94	110.94	105.42
50 % suc/lac	25	100.00	135.93	144.42	132.58	153.33	-
	30	100.00	133.12	135.21	138.10	141.74	140.52
	40	100.00	162.66	163.12	153.48	160.38	-
	50	100.00	147.31	150.83	165.76	152.71	-
50 % suc/whey	25	100.00	146.22	148.90	146.70	156.79	159.73
	30	100.00	137.75	139.25	159.59	159.78	149.18
	40	100.00	130.80	142.71	146.91	164.52	165.56
	50	100.00	145.27	148.67	147.15	164.50	158.00

Table 11.
(continuation) Percentage of initial solids content of osmotically treated apple samples[a]

Osmotic solution	Temp. (°C)	Time (hr) 0.0	0.5	1.0	2.5	5.0	6.0
25 % sucrose	25	100.00	129.44	131.59	133.20	135.70	156.24
	30	100.00	162.95	163.56	192.64	189.54	199.35
	40	100.00	166.97	164.73	169.67	191.59	208.96
	50	100.00	128.44	143.43	159.36	192.04	190.39
50 % sucrose	25	100.00	168.70	185.61	164.73	172.71	171.79
	30	100.00	152.48	163.24	169.33	166.40	197.64
	40	100.00	166.92	187.07	178.40	172.41	194.95
	50	100.00	169.39	164.86	189.20	205.72	221.12
25 % lactose	25	100.00	167.87	184.70	178.61	202.92	187.13
	30	100.00	177.01	255.46	202.92	229.67	202.15
	40	100.00	176.26	195.42	209.85	215.92	217.34
	50	100.00	190.69	293.00	237.02	194.41	217.13
25 % whey	25	100.00	140.28	126.46	149.36	147.33	139.12
	30	100.00	115.53	118.54	147.84	98.30	143.42
	40	100.00	128.49	129.51	129.62	132.93	141.60
	50	100.00	136.51	133.59	166.12	138.01	148.50
50 % suc/lac	25	100.00	165.70	164.90	185.14	165.76	185.39
	30	100.00	151.34	164.69	210.76	180.13	184.98
	40	100.00	181.26	115.18	196.63	220.43	204.51
	50	100.00	168.78	186.88	210.75	309.89	197.97
50 % suc/whey	25	100.00	148.85	142,67	146.53	157.26	162.71
	30	100.00	150.56	151.80	159.09	157.13	149.09
	40	100.00	141.71	145.74	150.72	179.39	154.23
	50	100.00	143.60	152.57	145.92	162.68	177.37

a - samples held to vacuum prior to contacting with osmotic solution.

Table 12. Solids content of osmotically treated apple samples (g solids / 100 g sample)

Osmotic solution	Temp. (°C)	Time (hr) 0.0	0.5	1.0	2.5	5.0	6.0
25 % sucrose	25	13.80	15.65	16.00	17.43	19.00	19.72
	30	13.80	16.54	17.30	17.61	24.41	22.41
	40	13.80	14.55	15.52	22.20	24.03	26.50
	50	13.80	16.61	18.96	24.14	29.64	31.98
50 % sucrose	25	13.80	19.19	21.50	22.90	26.95	27.53
	30	13.80	16.57	21.98	25.40	32.17	-
	40	13.80	20.60	22.52	27.96	36.51	48.67
	50	13.20	24.82	30.45	34.22	45.35	50.74
25 % lactose	25	13.80	20.16	18.01	15.66	17.10	17.54
	30	13.80	15.63	15.52	17.43	19.46	18.81
	40	13.80	16.16	16.68	17.27	18.18	18.53
	50	13.80	14.57	16.09	-	22.96	22.90
25 % whey	25	13.80	15.95	15.23	17.22	17.84	17.58
	30	13.80	15.90	15.31	16.81	17.10	17.34
	40	13.80	14.48	15.91	17.21	20.52	20.76
	50	13.80	15.30	16.85	20.78	23.21	23.65
50 % suc/lac	25	13.60	19.68	21.82	22.86	27.04	-
	30	13.60	19.62	21.21	26.36	30.71	32.92
	40	13.60	23.99	25.93	37.30	40.81	-
	50	13.60	23.12	25.57	42.18	45.75	-
50 % suc/whey	25	13.27	23.60	21.07	26.34	27.03	28.20
	30	13.27	19.51	20.43	26.34	27.80	29.18
	40	13.27	18.84	21.61	25.03	30.81	32.82
	50	13.27	20.65	25.56	32.57	43.05	52.24

Table 12.
(continuation) Solids content of osmotically treated apple samples (g solids / 100 g sample)

Osmotic solution	Temp. (°C)	Time (hr) 0.0	0.5	1.0	2.5	5.0	6.0
25 % sucrose	25	13.80	15.58	16.16	16.92	18.00	18.87
	30	13.80	17.37	18.89	20.15	20.43	21.41
	40	13.80	18.64	18.72	20.15	21.94	23.45
	50	13.80	16.49	17.71	21.15	27.94	29.06
50 % sucrose	25	13.80	22.35	24.41	26.74	29.82	30.82
	30	13.80	21.01	23.71	27.82	30.23	32.82
	40	13.80	22.98	30.45	31.35	34.48	38.73
	50	13.80	24.11	28.26	43.95	53.82	56.21
25 % lactose	25	13.60	18.33	18.79	18.85	21.14	20.84
	30	13.60	19.00	26.66	22.29	25.26	25.60
	40	13.60	18.69	20.63	23.07	25.32	26.62
	50	13.60	20.03	21.25	24.58	27.21	24.29
25 % whey	25	13.27	18.27	17.34	21.31	-	19.28
	30	13.27	15.80	16.36	21.31	27.17	27.00
	40	13.27	17.18	17.49	19.04	21.93	22.03
	50	13.27	17.73	18.58	24.23	22.55	24.87
50 % suc/lac	25	13.60	21.95	23.24	28.91	32.23	35.51
	30	13.60	21.78	23.35	30.65	35.67	41.27
	40	13.60	23.55	27.00	37.38	36.06	49.62
	50	13.60	24.78	29.22	41.37	51.57	54.18
50 % whey/suc	25	13.27	21.54	21.96	24.18	27.54	29.16
	30	13.27	21.39	22.87	27.87	31.53	36.43
	40	13.27	20.97	22.87	26.22	36.83	34.97
	50	13.27	21.49	27.69	33.66	44.68	46.99

Table 13. Mass transport coefficient (k) for osmotic preconcentration of apple samples based on normalized solids content, (hr^{-1})

Without vacuum contacting step

Osmotic solution	Temp. (°C)	k[a] (hr^{-1})	% increase of k[b]
25 % sucrose	25	0.17	-
	30	0.29	71
	40	0.40	135
	50	0.57	235
50 % sucrose	25	0.33	-
	30	0.55	67
	40	0.80	142
	50	1.14	245
25 % lactose	25	0.11	-
	30	0.15	36
	40	-	-
	50	-	-
25 % whey	25	0.08	-
	30	0.17	113
	40	0.23	188
	50	0.30	275
50 % suc/lac	25	0.28	-
	30	0.56	100
	40	0.89	218
	50	1.00	257
50 % suc/whey	25	0.33	-
	30	0.40	21
	40	0.57	73
	50	1.04	215

With vacuum contacting step

Osmotic solution	Temp. (°C)	k[a] (hr^{-1})	% increase of k[b]
25 % sucrose	25	0.12	-
	30	0.20	67
	40	0.25	108
	50	0.27	125
50 % sucrose	25	0.35	-
	30	0.20	67
	40	0.25	108
	50	0.27	125
25 % lactose	25	0.12	-
	30	0.29	142
	40	0.33	175
	50	0.36	200
25 % whey	25	-	-
	30	-	-
	40	-	-
	50	-	-
50 % suc/lac	25	0.57	-
	30	0.75	32
	40	1.11	95
	50	1.25	119
50 % suc/whey	25	0.36	-
	30	0.54	50
	40	0.59	64
	50	1.08	200

a - mass transport coefficient
b - from 25°C

Table 14. Organoleptic scores for osmotic preconcentrated freeze dried rehydrated apple samples.

Osmosis treatment	Taste scores [a]	Sig. [b]	Texture scores [a]	Sig. [b]
50 % suc/whey, 25°C, vacuum	7.17	A	6.42	A
50 % sucrose, 25°C	6.50	A	5.58	A
50 % suc/whey, 50°C	6.17	A	5.58	A
50 % suc/whey 25°C	5.67	A	5.50	A
None [c]	4.00	B	4.67	B
25 % whey, 50°C	3.08	B	4.17	B

a - nine (9) point Hedonic scale (9 = like extremely; 1 = dislike extremely)

b - samples having a different letter are different at a 1 % level of significance

c - freeze dried rehydrated apple samples, without pretreatment

Figure 6

Theoretical and experimental distribution of water within the apple sample.

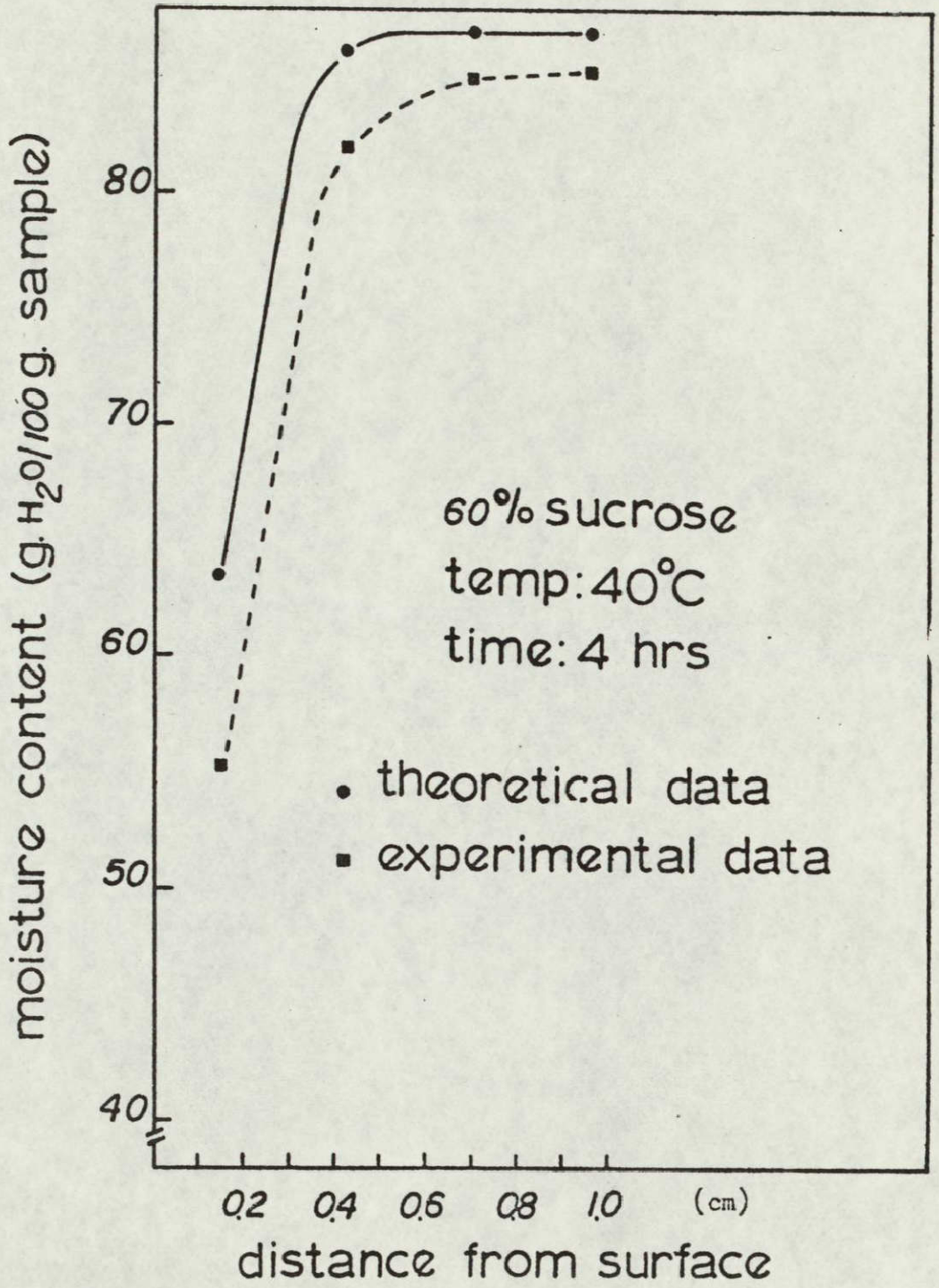


Figure. 7

Theoretical and experimental distribution of water within the apple sample

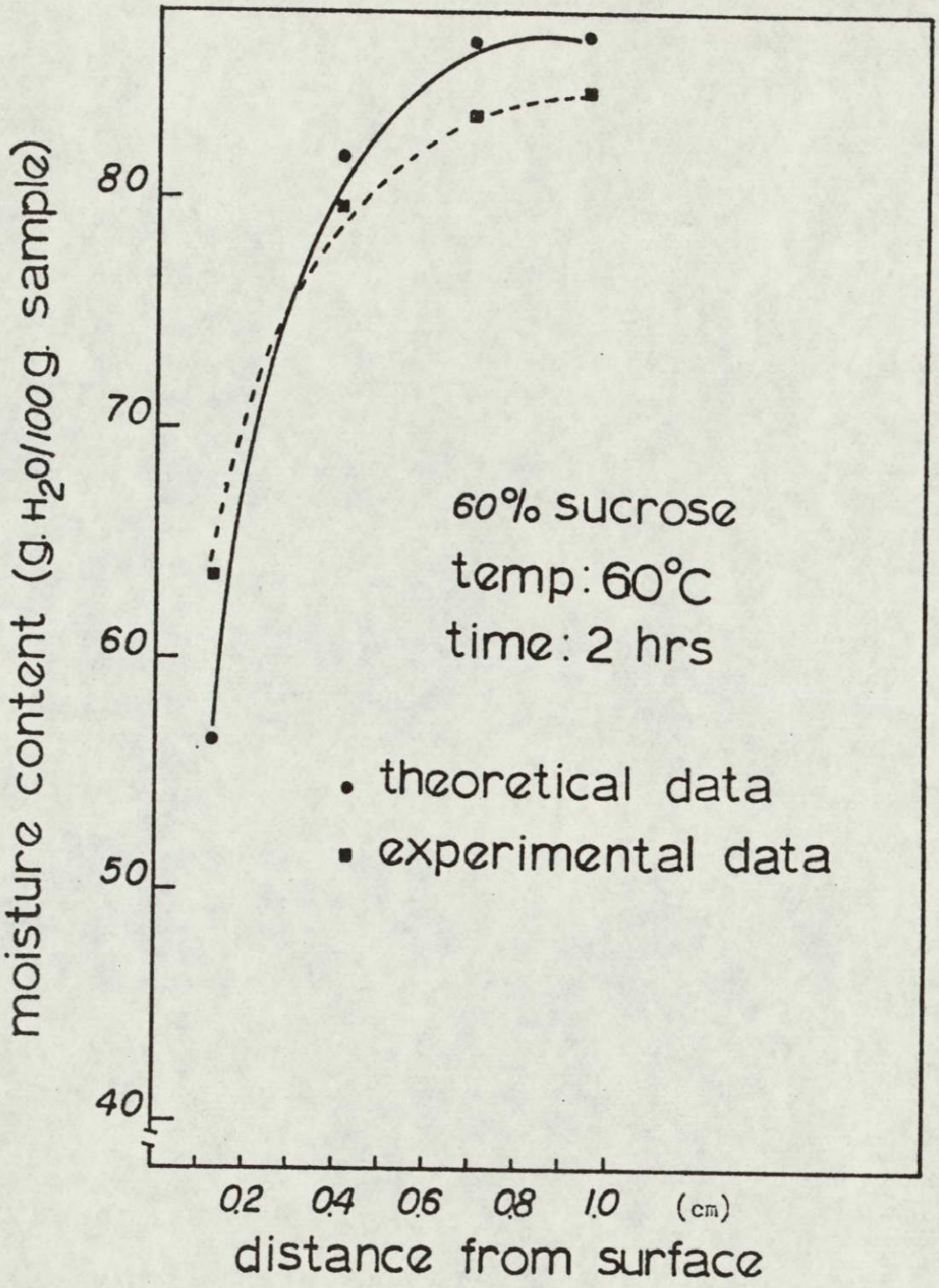


Figure 8

Relationship between calculated water diffusion coefficient temperature for osmotic dehydration of apples (60 % suc. soln.)

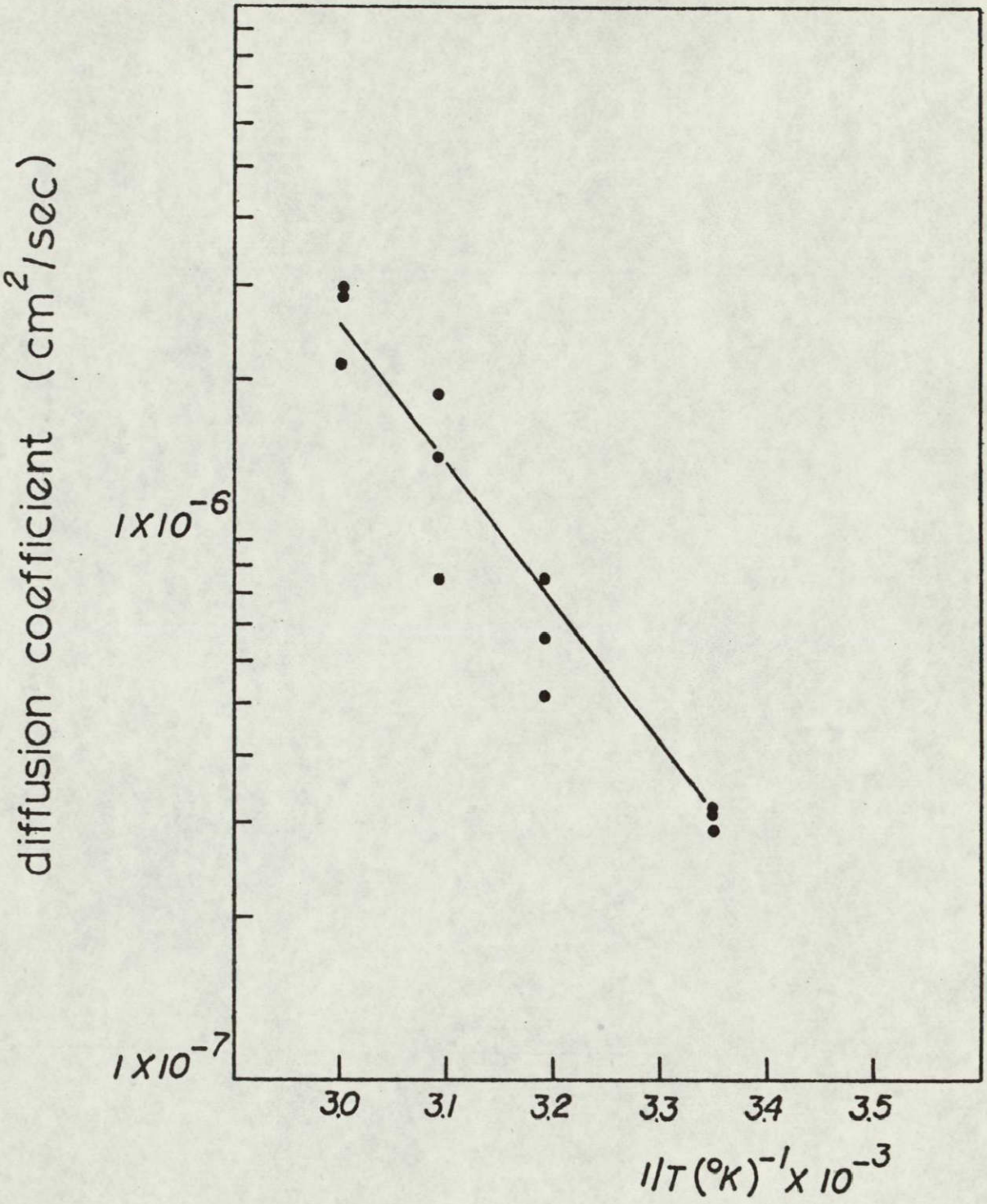


Figure 9

Film mass transfer coefficient for a 60 % sucrose solution as a function of temperature.

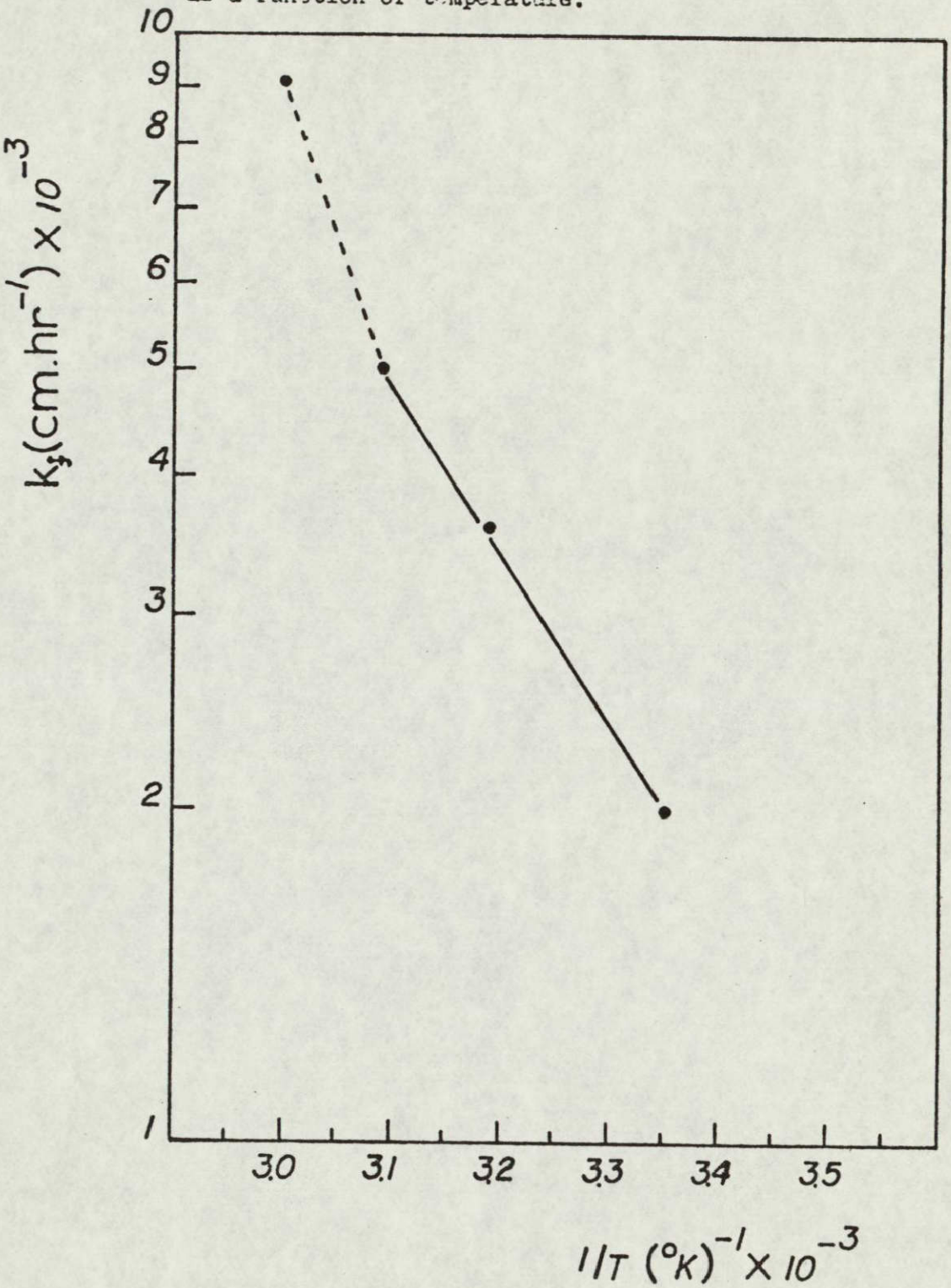


Figure 10

Percentage of original water content remaining after treatment with 25 % sucrose solution

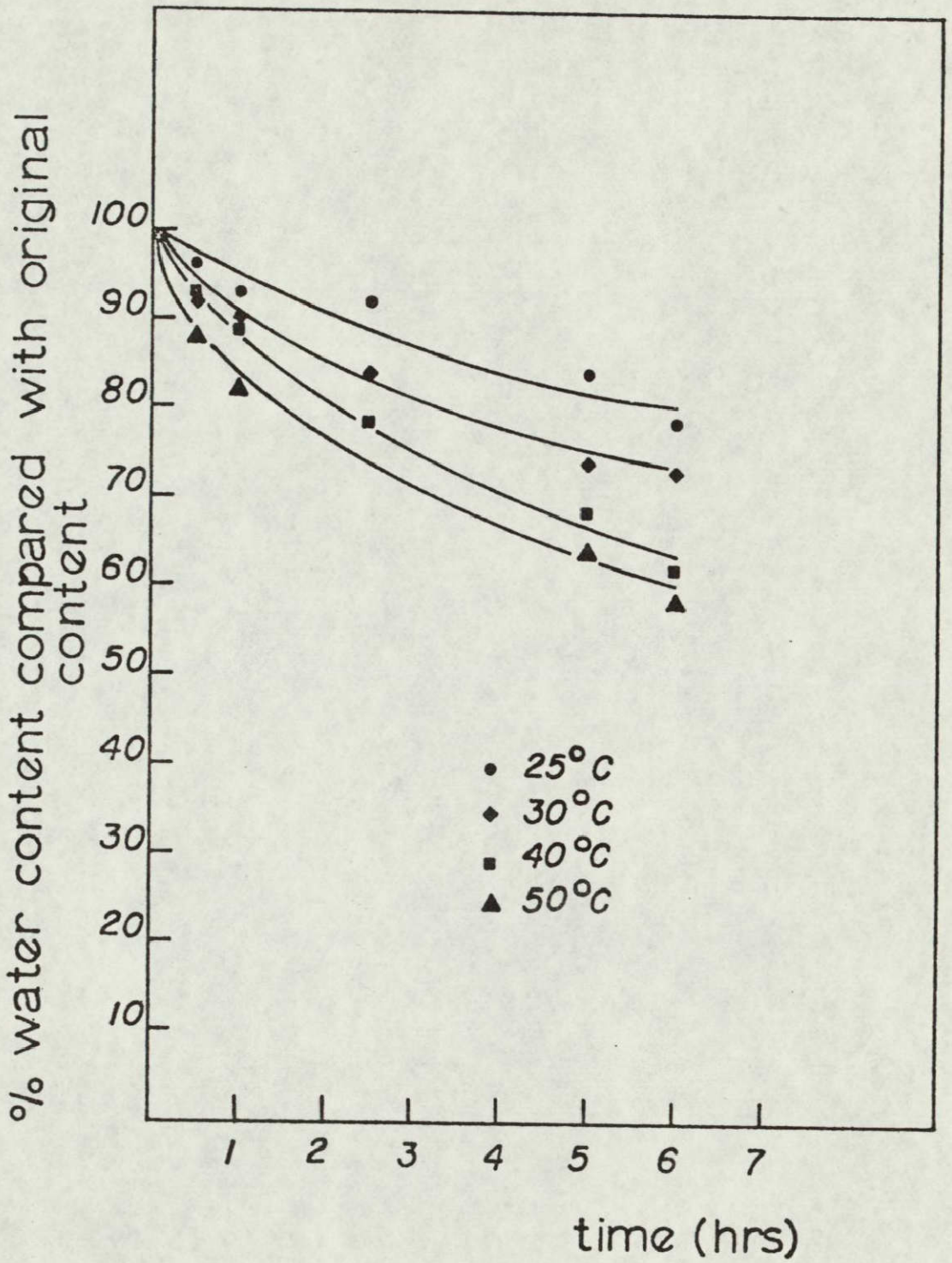


Figure 11

Percentage of original water content after treatment with 50 % sucrose solution.

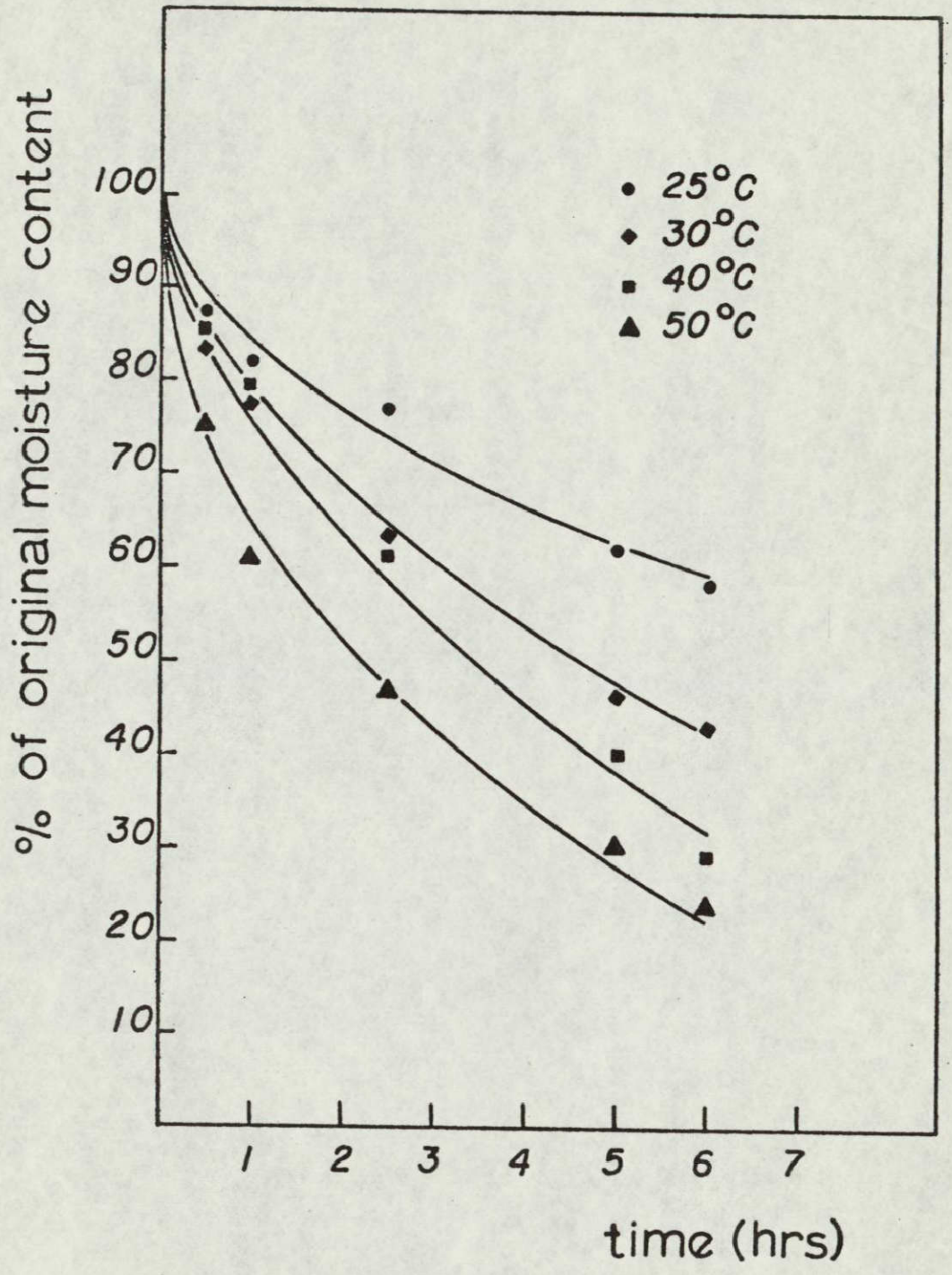


Figure 12

Solids content of apple samples treated with a 50 % sucrose/whey solution with vacuum contacting.

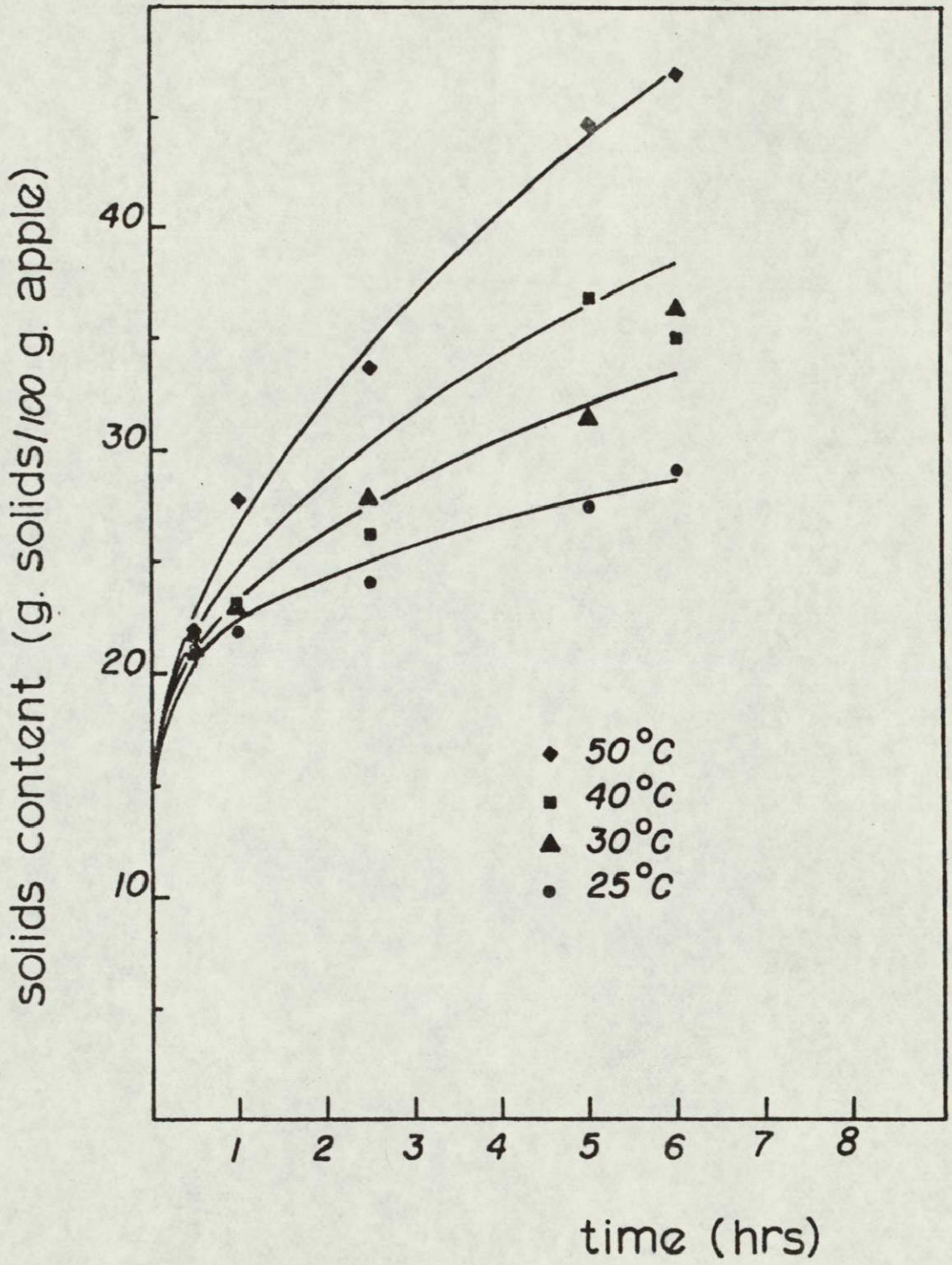


Figure 13

Normalized solids content as a function of square root of time in osmotically treated samples.

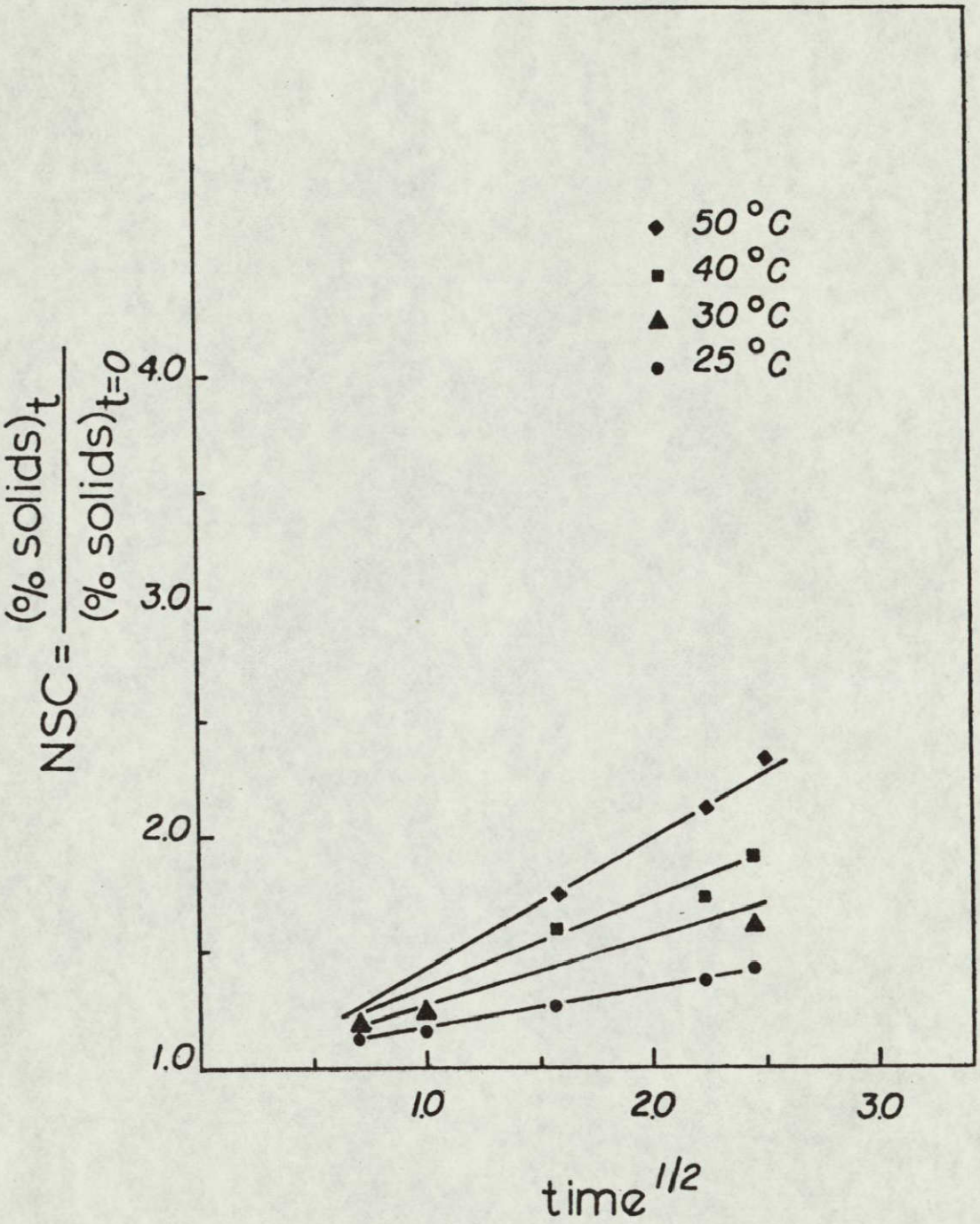
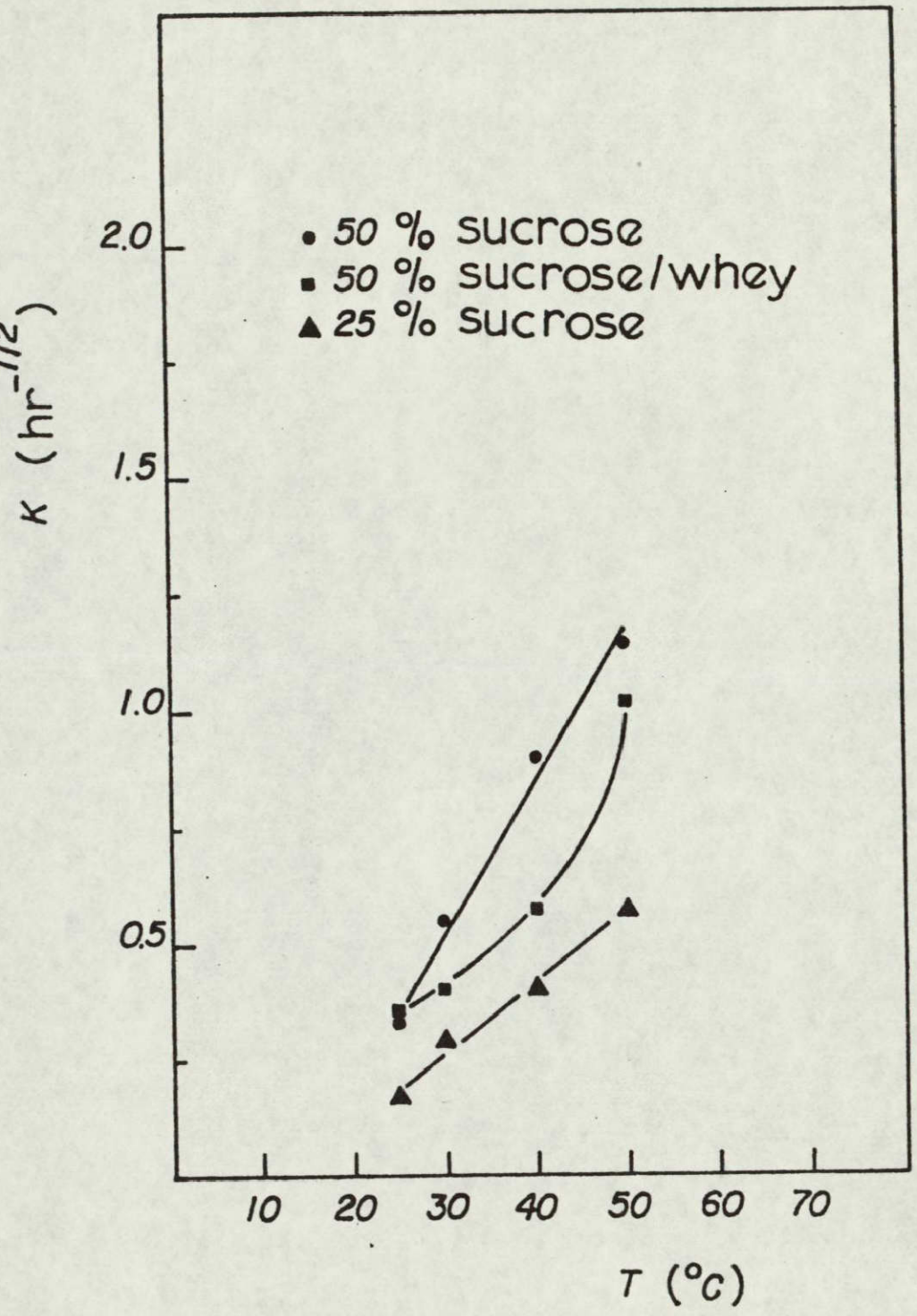


Figure 14

Mass transfer coefficient for solids uptake as a function of temperature for different osmotic solutions.



6. Summary of Results

1. Freeze-dried emulsion microstructure was studied by microscopic methods. The results obtained show that the fate of the oil phase is dependent on whether it can be incorporated in an amorphous solute or is excluded from it.

2. Egg albumin, gelatin, and carboxy methyl cellulose are among solutes which can provide amorphous structure upon freeze-drying and encapsulate oil, thus preventing it from physical loss and from oxidation deterioration.

3. Crystalline and insoluble solids are ineffective in encapsulating the oil.

4. Osmic acid staining allows observation correlation with macroscopic properties affected by the distribution of oil in the freeze-dried emulsions.

5. Various factors affecting "collapse temperature" were evaluated. These include composition, concentration of individual components, methods of freezing and drying, and conditions of storage.

6. Relation of the phenomenon of collapse to food deterioration processes such as caking, flavor release, stickiness, and others was discussed and applicability of our results emphasized.

7. Procedures for fabrication, characterization, and modification of textural properties of artificial food matrices were reported.

8. Factors which modified textural properties of the calcium alginate gel forming the AFM included added components such as pectin, gelatin, and sucrose.

9. Comparison of textural and sensory evaluations shows that sensory panelists could detect differences between samples which differed by more than 20 percent in mechanical properties.

10. A study was made of the distribution of calcium in the AFM, and it was concluded that the amount of the ion involved in formation of cross-linked junction zones depends only on alginate concentration but is not affected by presence of other components such as sucrose or pectin.

11. Two new freeze-dried products incorporating AFM were developed. They were a "nonfat dry milk vanilla pudding with AFM" and a "whole milk vanilla pudding with AFM." Both products were found to be organoleptically acceptable.

12. Osmotic concentration techniques for fruit using either pure or mixed osmotic systems were evaluated and found capable of producing acceptable products. The kinetics of the process were evaluated and reported.

13. The osmotic techniques were applied to osmotic concentration of vegetable products. Using a lactose/NaCl mixture it was possible to successfully treat carrots which could then be freeze-dried with sizable savings in drying capacity.

14. Osmotically treated carrots had a much improved storage stability.

15. The major potential defect of osmotically pretreated carrots was increased saltiness which was objectionable to some but not to all tasters.

16. An evaluation of sucrose, lactose, and whey as osmotic agents was prepared and reported.